Zeeman splitting and Faraday rotation associated with Mn$^+$ $^7P_J \leftarrow ^7S_3$ absorption: Photon-trap spectroscopy and quantum-theory analysis

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Abstract. A novel experimental method is presented for detection of a trace of optical absorption of mass-selected ions stored in an ion trap. Photon-trap spectroscopy (a generalized scheme of cavity ring-down spectroscopy) is the key technique, where a storage lifetime of photons in a high-Q cavity provides a ppm-level high sensitivity. Experiment was performed on the manganese ion, Mn$^+$, to record $^7P_{2,3,4} \leftarrow ^7S_3$ absorption spectra at around 260 nm. Zeeman splitting and Faraday rotation of the polarization plane were observed as well in the presence of a magnetic field. The high-resolution spectra show complex structures, which are fully interpreted by the quantum theory incorporating hyperfine interaction due to the Mn nuclear spin ($I = 5/2$). The present technique provides a novel approach to electronic and magnetic structures of mass-selected atomic, molecular, and cluster ions.

1. Introduction
We have developed a novel methodology for absorption spectroscopy of ions in the gas phase [1,2]. The technique combines an ion trap with an optical cavity. The ion trap enables high-density storage of ions. The cavity allows us to perform photon-trap spectroscopy [1–4] (a generalized scheme of cavity ring-down spectroscopy [5]) for achieving extremely high sensitivity to detect extinction of light through the stored ions; a storage lifetime of photons in the cavity provides absorbance measurement free from intensity fluctuation of the light source. It is thus possible to perform absorption spectroscopy of ions without relying on laser-induced fluorescence (LIF) or photodissociation, which are often employed for molecules and clusters [6]. The advantages of the present method over other techniques targeting ions in a discharge [7–9] are its capabilities for mass selection and for application of a magnetic field. The latter provides an opportunity for magneto-optical spectroscopy as well. We demonstrated so far the first experiment on the atomic ion of manganese, Mn$^+$ [1], and then size-selected cluster ions of silver, Ag$_9$ [2].

In the Mn$^+$ experiment [1], we reported absorption and magneto-optical spectroscopy, where three absorption spectra due to $^7P_{2,3,4} \leftarrow ^7S_3$ transitions were measured in the UV region along with their

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Zeeman splitting and Faraday rotation of the incident polarization plane. The stored Mn⁺ ions were even spin-polarized with the aid of the cavity by incidence of a circularly polarized laser pulse [10]. In this paper, we describe the experimental method briefly, and present theoretical analysis of the spectra. In particular, the role of hyperfine interaction is illustrated in the spectrum simulation.

2. Photon-trap spectroscopy of trapped ions

2.1. Experimental procedure

The major part of the experimental setup is shown in figure 1. Briefly, ions were mass-selected by a quadrupole mass filter, guided by octopole ion guides (IG) and a quadrupole deflector (QD), and stored in a 40-cm linear ion trap filled with a buffer He gas at room temperature. Optionally, the buffer gas can be cooled down by liquid He. About $1 \times 10^9$ mass-selected ions were trapped; the ion density was about $3 \times 10^9$ ions/cm³. The ion trap was located in a 10-cm bore of a 80-cm-long solenoidal superconductor magnet; the magnetic field was homogeneous over the ion trap volume within ±0.5%. The ions in the trap was further allowed to interact with photons trapped in a high-finesse optical cavity (a photon-trap cavity), which consisted of two mirrors (MR) with a reflectivity, $R = 99.98\%$, and a radius of curvature, $ROC = 6$ m, separated by 1.6 m.

The round-trip absorbance was evaluated with a precision better than 1 ppm from the lifetime of photons in the cavity, as measured by the intensity-decay rate of the signal pulse. For the measurement of polarization rotation, the signal pulse was split into two orthogonal polarization components [11]; the intensity difference between the two components is proportional to $\sin^2 \theta$, where $\theta$ is the angle of rotation. The angle, $\theta$, was determined with a precision of about 1 µrad, per round trip.

Figure 1. A schematic of the experimental setup. IGs: ion guides; QDs: quadrupole deflectors; MRs: cavity mirrors; PMTs: photomultiplier tubes.

Figure 2. (a) Energy-level diagram of Mn⁺. Vertical lines indicate allowed transitions. (b) Relative intensities of the transitions.

Figure 3. Absorption spectrum of the $^7P_4 \leftrightarrow ^7S_3$ transition of Mn⁺ without a magnetic field ($B = 0$ T). Solid circles: experimental data; bars: transition lines obtained theoretically; solid curves: spectrum simulation.
2.2. Results
The present experiment was performed on atomic ion of manganese, Mn⁺, which has a \(^7S_3\) ground state. By the measurements of the photon-trap lifetime as a function of the laser frequency, three absorption bands associated with spin-allowed electronic transitions \(^7P_J \leftarrow ^7S_3\) (\(J = 2, 3,\) and \(4\)) were observed at 38366.2, 38543.1, and 38806.7 cm \(^{-1}\), respectively, as reported by emission spectroscopy \[12,13\]. Here we present the results of the \(J = 4\) transition; relevant energy levels are illustrated in figure 2(a). An absorption spectrum measured is displayed in figure 3, which shows a hyperfine structure due to the nuclear spin of Mn (\(I = 5/2\)). The spectrum exhibited Zeeman splitting in the presence of a magnetic field of \(B = 3\) T as displayed in figure 4; the two panels show spectrum simulations performed in different levels of calculation as described in Section 3. A spectrum of Faraday rotation was measured as well, which is shown in figure 5.

3. Analysis of absorption and magneto-optical spectra
The hyperfine structure of the absorption spectrum at \(B = 0\) T was reconstructed from the transition energy (38806.689 cm \(^{-1}\)) and the hyperfine constants (\(A = 797.4\) and \(-122.9\) MHz for \(^7S_3\) and \(^7P_4\), respectively) reported by emission spectroscopy \[14\]. The bars in figure 3 (as well as figure 2(b)) indicate absorption lines satisfying the selection rule of \(\Delta F = 0\) and \(\pm 1\), where \(F\) is the quantum number of the total angular momentum (\(F = I + J\)). The lengths of the bars are proportional to the relative intensity. These absorption lines correspond to the 15 transitions shown in figure 2(a). The profiles of these absorption lines were added together after convolution with an instrumental function, dominated by the laser bandwidth of about 0.13 cm \(^{-1}\) \[1\], to obtain a simulated spectrum; the solid curve in figure 3 thus obtained explains the experimental data very well.

The spectrum of Zeeman splitting was simulated by the procedure outlined by Tremblay et al. for alkali-metal atoms \[15\]. Briefly, the magnetic field causes mixing among the levels with a different quantum number, \(F\), but with the same \(m_F\) via off-diagonal elements, \(\langle F^-1, m_F | H | F, m_F \rangle\), of the Hamiltonian, where \(H\) consists of unperturbed, hyperfine and Zeeman terms. The Hamiltonian was diagonalized to obtain eigenenergies and eigenfunctions both in the ground and in the excited states for calculation of transition energies and strengths.

![Figure 4](image-url)  
**Figure 4.** Zeeman splitting of the \(^7P_4 \leftarrow ^7S_3\) absorption spectrum of Mn⁺ at \(B = 3\) T. Solid circles: experimental data; bars: transition lines obtained theoretically; solid curves: spectrum simulation.  
(a) The simulation neglects hyperfine interaction; it does not account for the experiment perfectly.  
(b) The simulation incorporates hyperfine interaction, providing full explanation of the experimental data.

![Figure 5](image-url)  
**Figure 5.** Spectrum of Faraday rotation associated with the \(^7P_4 \leftarrow ^7S_3\) transition of Mn⁺ measured at \(B = 3\) T. Solid circles: experimental data; solid curve: spectrum simulation.
The spectrum shows splitting primarily by \( m_J \), as shown in figure 4(a), because the magnetic field is so strong as to be in the Paschen–Back regime. The selection rule, \( \Delta m_J = \pm 1 \), provides 7 lines for each component of blue- and red-shifts. However, the simulated spectrum does not agree with the experimental data; the peaks observed in the experiment do not show a regular interval, and even shoulder structures are discernible (for example, at 38805.3 and 38808.0 cm\(^{-1}\)). Actually, these 14 lines are subject to further splitting by hyperfine interaction; each line splits into 6 due to \( m_I = -5/2, ..., +5/2 \) with a selection rule, \( \Delta m_I = 0 \). These 84 lines reproduced every detail of the experimental spectrum as shown in figure 4(b). The interval of the hyperfine splitting is dependent on the value of \( m_J \), and thus a different magnitude of broadening is caused for the 14 lines.

The spectrum of the Faraday rotation was simulated as well. Each transition line of the Zeeman splitting was represented by a dispersion profile. They were added together for blue- and red-shifted components separately after convolution with the instrumental function. The difference of these two dispersion profiles is proportional to the magnitude of the polarization rotation, which is shown by the solid curve in figure 5. The experimental spectrum was fully reproduced by this simulation.

4. Summary
We have shown that absorption and magneto-optical spectra of mass-selected ions can be measured by our novel technique combining an optical cavity and an ion trap. The spectra of field-free absorption, Zeeman splitting and Faraday rotation measured for the atomic ion of manganese, Mn\(^+\), were fully explained by the simulation based on the quantum theory of atomic transitions incorporating hyperfine interaction. Extension of the present magneto-optical spectroscopy toward cluster ions would provide clear evidence for specificity of their magnetism; Mn\(_2^+\) and Mn\(_3^+\) are considered to exhibit a ferromagnetic spin coupling in contrast to antiferromagnetic bulk manganese [6,16,17].

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