Photon-trap spectroscopy of mass-selected ions in an ion trap: Optical absorption and magneto-optical effects

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A novel experimental technique has been developed to observe a trace of optical absorption of free mass-selected ions. The technique combines a linear radio-frequency ion trap with a high-finesse optical cavity to perform cavity ring-down spectroscopy (photon-trap spectroscopy for generality), where the storage lifetime of photons in the cavity provides a sensitivity high enough to probe the trapped ions. Absorption spectra of the manganese ion Mn⁺ are presented, showing hyperfine structures for the $^7P_{2,3,4} \rightarrow ^5S_{3/2}$ transitions in the ultraviolet range. Implementation of a solenoidal magnet allows us to observe the Zeeman splitting and the Faraday rotation as well. © 2007 American Institute of Physics. [DOI: 10.1063/1.2822022]

Development of cavity ring-down spectroscopy (CRDS) has enabled optical absorption measurements with a considerable advantage over conventional transmission spectroscopy in sensitivity. The technique exploits a lifetime of photons stored in a high-finesse optical cavity enclosing a sample material. It has been widely used in gas-phase spectroscopy, and is now applied even to solid substrates and liquids in a cell, with a variety of modified schemes. The back-and-forth propagation of the light during multiple reflection represents a simple picture of CRDS in the time domain, while the lifetime is derived more generally as a resonance property of a cavity in the frequency domain. This extended consideration of CRDS leads us to introduce a term “photon-trap spectroscopy” for generality.

Gas-phase spectroscopy of free ions of atoms, molecules, and clusters can be performed in a well-defined experimental condition by using an ion trap, which affords an opportunity to control various parameters such as an isotope and an elemental composition by mass selection, a temperature by buffer-gas thermalization, a density, an external field, etc. In particular, a linear-multipole radio-frequency (rf) ion trap developed for ion chemistry has recently been applied to photodissociation spectroscopy of size-selected molecular and cluster ions under a controlled temperature. The technique is unique for ion spectroscopy as well because of its potential for high resolution and high-density storage of selected ions. Difficulties in absorption spectroscopy of ions have been overcome by elaborate techniques. For example, velocity-modulation spectroscopy has been developed for molecular ions in a discharge, and for an atomic ion in a Paul trap. CRDS was first applied to high-density ions generated by a hollow-cathode discharge.

In this Communication, we report absorption spectroscopy of the atomic ion of manganese Mn⁺ as the first application of the experimental method developed. In addition, magneto-optical spectroscopy is performed to observe the Zeeman and the Faraday effects. The spectra measured are analyzed theoretically by referring to the hyperfine structures reported by emission spectroscopy. The prospect of the technique for application to molecular and cluster ions is discussed on the basis of an optical sensitivity achieved and an ion-density distribution in the trap evaluated.

The experimental setup is shown in Fig. 1. Ions are generated in the magnetron-sputter (cluster) ion source, guided by octopole ion guides (IG1–4) driven by homemade rf generators, bent by quadrupole deflectors (QD1, 2), and mass selected by a quadrupole mass filter (QM1) (MAX-4000, Extrel CMS). The mass filter selects not only an isotope but also a size of clusters. The mass-selected ions, with a typical current range of 0.1–1 nA, are admitted into a 40 cm linear octopole ion trap (IG5) filled with buffer He gas at a controlled temperature between 300 and 8 K, which decelerates and thermalizes the ions. The number of ions stored, as measured by a current detector (ID) of extracted ions, is reproducible within ±2% in a given condition of trap.
voltages and ion-beam intensity, whereas the maximum number stored varies in the range of $10^8$–$10^9$ (an average ion density of $10^6$–$10^7$ ions/cm$^3$) depending on the conditions. The stored ions interact with photons trapped in a high-finesse optical cavity (a photon-trap cavity), consisting of two mirrors (MR1, 2) with a 6 m radius of curvature separated by 1.6 m, where a tunable 5 ns laser pulse is injected from an optical parametric oscillator equipped with a frequency doubler (MOPO-HF, Spectra Physics) at a repetition rate of 10 Hz with a typical pulse energy of 2 $\mu$J. An output signal pulse is detected by a photomultiplier tube and its temporal profile is processed to obtain the storage lifetime of photons. In a typical procedure, we first load the ions and record the lifetime for 20 shots, second eject the ions and record the lifetime of an empty cavity for 20 shots, and then repeat this set of measurements five times. The difference in the light extinction rates (a reciprocal of the lifetime) averaged for ions on and off, which is proportional to the absorbance, is recorded as a function of the laser frequency to obtain the storage lifetime of photons. The absorbance per round trip or better depending on the reflectivity of the cavity mirrors available.

Additionally, a magnetic field is applied to the trapped ions by an 80-cm-long solenoidal superconductor magnet (Japan Superconductor Technology, Inc.); the magnetic field is variable between 0 and 5 T and is homogeneous through the ion-trap volume within $\pm 0.5\%$. Change in the ion trajectory due to the magnetic field is compensated for by vertical electric deflectors (VD1, 2). Not only optical absorption but also rotation of the polarization plane can be measured with additional optical elements: a polarizer for the incident light to prepare linear polarization at an arbitrary angle and an analyzer for the signal light to separate two polarization components.\(^{21,22}\) An intensity difference between the two components is proportional to $\sin 2\theta$ ($\theta$ the angle of rotation), whereas a sum of them gives a signal of absorbance. (A quarter-wave plate $\lambda/4$ is for experiments with a circularly polarized light, which is not used in the present study.) Implementation of these elements allows us to measure spectra of the Zeeman splitting and the Faraday rotation simultaneously.

The spin-allowed electronic transitions of Mn$^+$ from the $^7S_3$ ground state to the $^7P_J$ ($J=2$, 3, and 4) excited states locate at wavelengths of 260.568, 259.372, and 257.610 nm, respectively.\(^{15}\) Therefore, the present cavity mirrors were designed to make the reflectivity $R$ at 260 nm as high as possible; $R=99.98\%$ was achieved. The storage lifetime of photons was 26.67 $\mu$s ($\tau_0$) for an empty cavity: $\tau_0=(d/c)/(1-R)$, where $d=1.6$ m is the cavity length and $c$ is the velocity of light in a vacuum. The lifetime was reduced to $\tau$ in the presence of absorbents; absorbance per round trip $A_\lambda$ is given by $(2d/c)(1/\tau-1/\tau_0)$. For example, $\tau=26.02$ $\mu$s when $A_\lambda=10$ ppm. This mirror coating provided a noise level in $A_\lambda$ of about 1 ppm; otherwise, it was as large as 70 ppm with lower reflectivity ($R=99.2\%$).

The absorption spectra of Mn$^+$ in the vicinities of the three transitions $^7P_J\leftarrow^7S_3$ ($J=2$, 3, and 4) are shown in Figs. 2(a), 2(a$'$), and 2(a$''$), respectively, which were measured by the ion trap at room temperature. Each spectrum shows a hyperfine structure (HFS) due to the nuclear spin of Mn ($I=5/2$). The profiles of the spectra are simulated, as will be described later. The energy resolution is currently limited by the linewidth about 0.1 cm$^{-1}$ of the laser, which is larger than the Doppler broadening at the room temperature; the spectral profiles did not change much even at 8 K.

Each absorption line exhibited splitting under a magnetic field by the Zeeman effect with a magnitude proportional to the strength $B$ of the field. The spectra measured at $B=3$ T are shown in Figs. 2(b), 2(b$'$), and 2(b$''$) for the transitions to $J=2$, 3, and 4, respectively. The spectral shape is sharp for the transition to the $J=3$ state, whereas several separated peaks are discernible in the spectra of $J=2$ and 4. The spectra of Faraday rotation measured simultaneously are shown in Figs. 2(c), 2(c$'$), and 2(c$''$), which exhibit peak structures.
more clearly in J=2 and 4. These spectra are explained by the simulation, which will be described later.

The absorption spectra at B=0 T are simulated by referring to the transition energies of the HFS components reported. The HFS-free transition energies are 38 366.227, 38 543.122, and 38 806.689 cm⁻¹ for transitions to J=2, 3, and 4, respectively; the A constants of HFS due to the magnetic dipole interaction are 797.4, −524.6, −143.9, and −122.9 MHz for \( ^3S_1 \), \( ^3P_2 \), \( ^3P_3 \), and \( ^3P_4 \), respectively, and the B constants due to the electric quadrupole interaction are zero for all the states. The transitions calculated are indicated by bars in Figs. 2(a), 2(a’), and 2(a’’). The magnitude of the secondary splitting by \( m_I \) is superimposed on the data, as shown in Figs. 2(a), 2(a’), and 2(a’’). The peak structures are reproduced even for blue- and redshifted components, which is agreement with the experimental results. The absorption spectra at B=3 T are indicated by bars in Figs. 2(b), 2(b’), and 2(b’’). The intensity ratio of the transitions to J=2, 3, and 4 thus obtained from the experimental results is 5:9:6:9:9:0, which agrees well with the theoretical prediction of 5:7:9.

The spectra of Zeeman splitting are simulated by the procedure outlined by Tremblay et al. for alkali-metal atoms. The transition energies and strengths calculated for B=3 T are indicated by bars in Figs. 2(b), 2(b’), and 2(b’’). The vertical and horizontal scales are shown by solid curves in Figs. 2(b), 2(b’), and 2(b’’). The absorption strength gives an oscillator strength, if once the absorption strength is known. However, we have a difficulty in evaluating the oscillator strength because ions in the trap may be distributed inhomogeneously. Therefore, we estimate the local density \( \rho_{local} \) of Mn⁺ ions in the laser interaction region, in the other way round, by referring to the oscillator strengths reported: 0.20, 0.28, and 0.36 for J=2, 3, and 4, respectively.\(^{15}\) It was found that \( \rho_{local} \) is not proportional to the total number of ions, \( N \), loaded in the trap; for example, \( \rho_{local} \) increased only by a factor of 2 from 0.5×10⁷ to 1×10⁷ cm⁻³, even when \( N \) was raised by one order of magnitude from 0.2×10⁹ to 2×10⁹ corresponding to an average density \( \rho_{av} \) of 0.5×10⁷ and 5×10⁷ cm⁻³, respectively. It is
speculated that ions are located more at the edge of the trap than at the center in high ion-loading conditions.

On the basis of these observations, we point out that the distribution of ions is inhomogeneous and is dependent on the operation condition of the ion trap. Therefore, a detailed study of ion distribution is needed to evaluate an absolute absorption cross section. It is estimated to be about $10^{-16}$ cm$^2$, provided that a density of ions is $1 \times 10^7$ cm$^{-3}$ and an optical sensitivity is 0.1 ppm, as achieved in the visible range with cavity mirrors of high reflectivity ($R=99.995\%$). This evaluation ensures detection of electronic transitions of molecules and clusters.

Finally, we mention the prospects for the minimum detectable absorption cross section. It is estimated to be about $1 \times 10^{-16}$ cm$^2$, provided that a density of ions is $1 \times 10^7$ cm$^{-3}$ and an optical sensitivity is 0.1 ppm, as achieved in the visible range with cavity mirrors of high reflectivity ($R=99.995\%$). This evaluation ensures detection of electronic transitions of molecules and clusters.

In conclusion, we have developed a technique for absorption and magneto-optical spectroscopy of mass-selected ions in a trap in combination with photons stored in a cavity. The experiment was demonstrated for the manganese ion; spectra of hyperfine structures, the Zeeman splitting, and the Faraday rotation were measured and were analyzed theoretically. Characterization of the ion-storage density and the optical sensitivity provides promising features for its application to electronic spectroscopy of molecular and cluster ions. We plan to apply this technique to size-selected cluster ions of manganese to investigate their size-dependent magnetism.26–28

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23For example, H. E. White, Introduction to Atomic Spectra (McGraw-Hill, New York, 1934).