PHYSICAL REVIEW A VOLUME 55, NUMBER 1 JANUARY 1997

Production of YbH^+ by chemical reaction of Yb^+ in excited states with H_2 gas

Kazuhiko Sugiyama and Jun Yoda
National Research Laboratory of Metrology, 1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan

(Received 9 May 1996; revised manuscript received 22 August 1996)

It is known that fluorescence of trapped Yb^+ ions fades with continuous driving of the $^2S_{1/2}$-$^2P_{1/2}$ transition in the presence of buffer gases. This phenomenon has been interpreted as being caused by population trapping in the $^2F_{7/2}$ state of Yb^+. As another cause of the fluorescence disappearance, we found the production of YbH^+ by chemical reaction of Yb^+ in excited states with H_2 gas. We found that the wavelengths of 369.482, 369.202, and 368.947 nm, formerly assigned as wavelengths for deexcitation of Yb^+ in the $^2F_{7/2}$ state to the $^2S_{1/2}$ ground state, are actually photodissociation lines of YbH^+. The change of the resonance point of rf resonance absorption signals indicates the production and dissociation of YbH^+ ions. The production of YbH^+ may be a problem in establishing frequency standards using buffer-gas-cooled Yb^+, owing to difficulty in removing H_2 gas from vacuum systems. [S1050-2947(97)50301-5]

PACS number(s): 33.80.Gj, 34.50.Lf, 32.80.Bx

I. INTRODUCTION

The ion trap technique is one of the candidates for use in future frequency standards [1]. Collisional cooling with light buffer gases is used in microwave frequency standards using rf traps to reduce the second-order Doppler shift that is a source of uncertainty [2]. Yb^+ is one of the attractive ion species that provide reference transitions in both microwave and optical frequency standards [1]. In the microwave region, buffer-gas-cooled $^{171}Yb^+$ has been investigated to establish a new frequency standard [3,4]. In the presence of buffer gases, however, fluorescence of trapped Yb^+ ions fades when the $^2S_{1/2}$-$^2P_{1/2}$ transition is continuously driven [5–11]. Researchers in Hamburg were the first to recognize this phenomenon and explained that it was caused by population trapping in the $^2F_{7/2}$ state, the lifetime of which exceeds 8 days [5]. After that, the pressure dependence of the fluorescence decay time was observed by Klein *et al.* [6], and Bauch *et al.* concluded that the population trapping was induced by collision with buffer gases [7]. The partial term scheme of Yb^+ related to this paper is shown in Fig. 1.

As another reason for the fluorescence decay, here we report the production of YbH^+ by chemical reaction of Yb^+ in excited states with H_2 gas. We have found that some observations formerly interpreted to be associated with Yb^+ in the $^2F_{7/2}$ state are actually caused by YbH^+. To investigate the production of YbH^+, we have detected trapped ions mass-selectively by combining a quadrupole mass analyzer with our rf trap.

In previous papers, we suggested the possibility of the production of molecular ions by chemical reaction of Yb^+ in excited states with background gases [8], especially O_2 and H_2O gases [9]. This proposal arose from the investigations to clarify the cause of our observation that rf resonance absorption signals (rf signals) were shifting in their resonance point toward one of heavier mass and then finally disappearing, while the fluorescence faded [10,11]. In Refs. [8,9], the disappearance and shifting of rf signals had a slower time constant than the fluorescence decay did; however, the production of YbH^+, reported here, occurs in the same time scale as the fluorescence decay. We overlooked the YbH^+ production by confusing it with population trapping in the $^2F_{7/2}$ state [8,9], as was done in other laboratories. As for a related observation, Seidel and Maleki recently conjectured the possibility of formation of molecular ions based on their observations with continuous driving of the $^2S_{1/2}$-$^2P_{3/2}$ transition [12].

II. EXPERIMENTAL SETUP

The experimental setup is shown in Fig. 2. We used the same rf trap as that previously used [8–11]. The inner diameter of the ring electrode was 22.6 mm. One of the endcap electrodes was made of mesh and was used to extract ions from the trap to transfer them to a quadrupole mass analyzer. Parameters of the trap, the detection method of rf signals, and the uv beam were the same as those described in Ref. [9] to enable comparison of the previous results. The amplitude and frequency of the trapping ac voltage were 310 V and 550 kHz, respectively. When we did not detect rf signals, the trapping dc voltage (V_{dc}) was fixed to 8.0 V. When we detected them, V_{dc} was modulated into a triangular wave from 5.2±1 V to 11.2±1 V with a period of 60–62 s, while the frequency of the probing rf field was fixed at 83.5 kHz. The trap was placed in a vacuum chamber evacuated by an ion pump. Yb^+ ions were produced inside the trap by electron bombardment of neutral Yb vapor, generated using an oven.

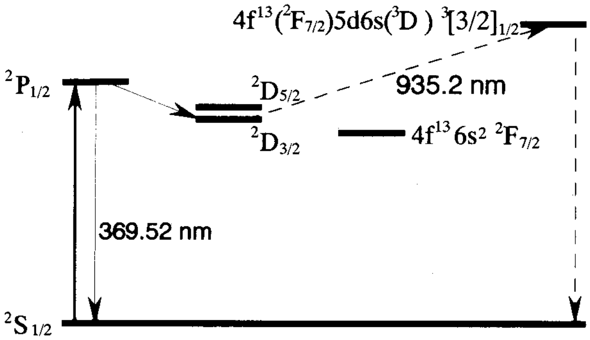

FIG. 1. Partial energy term scheme of Yb^+.

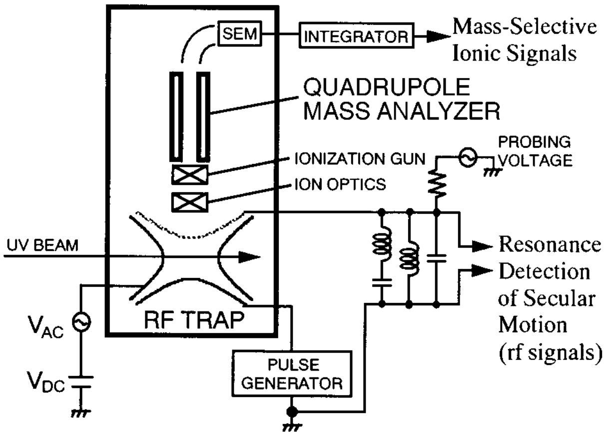

FIG. 2. Experimental setup.

The total pressure was measured using a nude Bayard-Alpert gauge. The background pressure was below 1×10^{-7} Pa and 5×10^{-7} Pa with the oven and electron gun off and on, respectively. The power of radiation at 369.52 nm, produced by second-harmonic generation from dye-laser (Spectra Physics 380D) radiation with an external cavity technique, was set to 16 μW at a window of the chamber. The beam size was 2 mm×2 mm at the center of the trap. The frequency of radiation at 369.52 nm was set to the resonant frequency of the investigated isotope by detecting the absorption signals of Yb^+ in a lamp.

We placed a quadrupole mass analyzer (Balzers QMG421C-3) above the mesh endcap electrode. The ions stored in the trap were expelled by a pulsed voltage of 50 V applied between the two endcap electrodes. This voltage was higher than the axial pseudopotential depth of 19 eV and sufficient for expelling the trapped ions. Then, ions of a specific atomic mass passed through the mass analyzer and were detected by a secondary electron multiplier (SEM) followed by an integrator and a peak holder. A similar mass-selective ionic detection system was developed by Matsuo *et al.* [13]. Our mass analyzer had a resolution below 1 atomic mass unit (amu) between 1 and 400 amu, and an ionization gun set in front of the quadrupole rods. This allowed us to measure the relative partial pressure of background gases. We calibrated the mass spectrometer for absolute amu and resolution below 1 amu around 174 amu by detecting neutral Yb from the oven.

III. RESULTS

Trapped Yb^+ ions were prepared by the following procedure. After the oven and the electron gun were turned on and the temperature of the oven reached equilibrium, we introduced gases into the vacuum chamber. About 15 min was required for stabilization of the total and partial pressures of gases. In order to load the same number of trapped Yb^+ ions in a series of measurements, we fixed the time during which Yb^+ ions were being loaded, i.e., we switched off the trapping ac voltage for a short time, switched it on again, and after 5 min, turned off the oven and electron gun. After the oven was sufficiently cooled, we started irradiating the Yb^+ ions with uv radiation. The number of Yb^+ ions loaded was of the order of 10^5 and 10^4 at a He pressure of 8.5×10^{-5} Pa and a H_2 pressure of 4×10^{-6} Pa, respectively. The equivalence of the load-to-load number was checked by the fact that rf signals were in the same size and shape. At a H_2 pressure of 4×10^{-6} Pa, until the oven cooled, the number of trapped Yb^+ ions decreased to the minimum detectable number by rf signals. After the oven cooled, however, the decay time of the number was negligibly slow. We checked this by detecting the fluorescence of trapped Yb^+ ions before we introduced the mass analyzer. We assumed that this initial decrease of the number was the same in the load-to-load case.

We detected mass-selective signals at 177 amu at a total pressure of 4×10^{-6} Pa composed of 99% H_2 gas after we irradiated Yb^+ ions with radiation at 369.52 nm for 1 min. We checked, without irradiation at 369.52 nm, that no signals were detected at 177 amu. We used a natural isotope mixture of 168-, 170-, 171-, 172-, 173-, 174-, and 176-amu isotopes of Yb. Therefore, it is possible that signals at 177 amu represent ions between (176+1) amu and (168+9) amu. We searched the signals between 177 and 185 amu, which corresponded to ions between (176+1) amu and (176+9) amu, to resolve the ambiguity, and found that signals were detected only at 177 amu. Therefore, signals at 177 amu represent the ions at (176+1) amu, i.e., $^{176}YbH^+$.

We found that YbH^+ was photodissociated by radiation at the wavelengths formerly assigned to deexcitation lines of Yb^+ in the $^2F_{7/2}$ state to the $^2S_{1/2}$ ground state. Bauch *et al.* determined the four wavelengths for the deexcitation lines and found that these wavelengths were not in agreement with those expected from tabulated energy levels of Yb^+ [7]. We confirmed the photodissociation of $^{174}YbH^+$ ions with irradiation at three of the four wavelengths, i.e., 369.482, 369.202, and 368.947 nm. In Fig. 3, we show the wavelength dependence of the photodissociation of $^{174}YbH^+$ ions. At present, a large scattering of signal height in each measurement of our mass-selective detection only allows us to judge whether the signals can be detected or not. However, we observed that signals of $^{174}YbH^+$ ions were below the detectable level around the center wavelengths determined in Ref. [7].

We also observed that $^{174}Yb^+$ ions were recovered by photodissociation of $^{174}YbH^+$ ions by detecting the signals at 174 amu after irradiation at around 369.482 nm. (We checked that the signals at 174 amu could not be detected after irradiation at 369.52 nm.) We could not obtain a strong wavelength dependence as shown in Fig. 3. Even if the wavelength is away from the center of the photodissociation line, photodissociation may occur at a slower rate and the number of dissociated Yb^+ ions reach the detectable level. However a large scattering of signal height in each measurement prevented us from obtaining the profile of the line.

Even when we introduced only He gas into the chamber to a total pressure of 8.5×10^{-5} Pa, we obtained mass-selective signals of YbH^+ with irradiation at 369.52 nm and a photodissociation spectrum at around 369.482 nm, similar to those in Fig. 3(a). We analyzed the composition of gases in the chamber and found that the pressure of H_2 gas increased as the pressure of He gas increased. At a total pressure of 8.5×10^{-5} Pa, the composition of gases was 86% He,

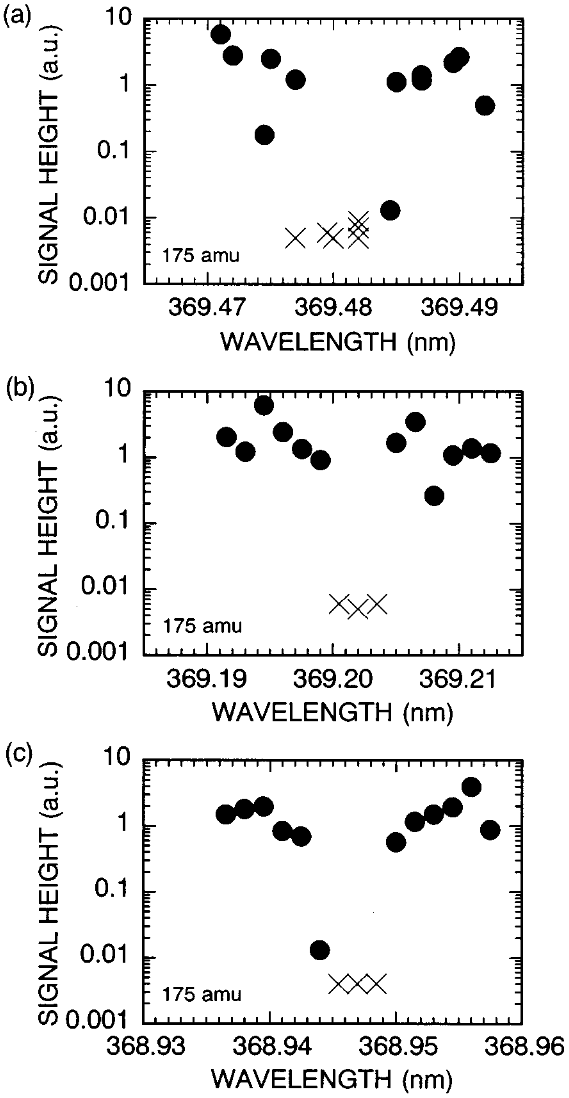

FIG. 3. Mass-selective signals of trapped ions at 175 amu after irradiation at around (a) 369.482 nm, (b) 369.202 nm, and (c) 368.947 nm. We irradiated $^{174}Yb^+$ ions first at 369.52 nm for 2 min to produce $^{174}YbH^+$ ions (without irradiation at 369.52 nm, no signals were detected at 175 amu), and then we switched the uv wavelength to that indicated in the abscissa. After 10 s of irradiation, we applied a pulsed voltage to transfer the trapped ions to the mass analyzer. At the wavelength where we could not detect the signals, we indicated the noise level at the time of detection by ×. (a.u., arbitrary units.)

13% H_2, and 1% others. This may be one reason why YbH^+ formation was overlooked in previous work, including ours. The purity of the He gas used was 99.995%; therefore, H_2 gas was produced or mixed somewhere in the whole vacuum system.

IV. DISCUSSION

YbH^+ is produced from Yb^+ in excited states by

$$Yb^{+*}+H_2 \rightarrow YbH^+ + H. \qquad (1)$$

When the $^2D_{3/2}$ state is optically depleted, even in the presence of buffer gases, it is not observed that fluorescence of Yb^+ ions fades [8,14]. Therefore, reaction (1) occurs when Yb^+ is in the $^2D_{3/2}$ state (2.85 eV). Or, if population trapping in the $^2F_{7/2}$ state occurs (see below) and the proposed path, i.e., fine-structure mixing collision between the $^2D_{3/2}$ and $^2D_{5/2}$ states and subsequent spontaneous decay from the $^2D_{5/2}$ to $^2F_{7/2}$ states [7,15] is true, there is a possibility that reaction (1) occurs in the $^2F_{7/2}$ (2.66 eV) and/or $^2D_{5/2}$ (3.02 eV) states.

To our knowledge, the dissociation energy D_0 of YbH^+ has not been measured. Because the reacted Yb^+ should have an internal energy below 3.02 eV and $D_0(H_2)$ of 4.478 eV [16], we estimate $D_0(YbH^+)$ to be greater than 1.5 eV. The known dissociation energies of metal-hydride ions range from 0.7 to 3.2 eV [17]. Even if the produced YbH^+ keeps all of the excess energy after reaction (1) as its internal energy, its photodissociation requires an energy greater than that obtained from $[D_0(H_2)-(\text{energy of } Yb^+ \text{ at reaction (1)})]$. We estimate this value to be 1.6 eV, assuming that reaction (1) occurs in the $^2D_{3/2}$ state and ignoring kinetic energy. Radiation at 369.48 nm (3.36 eV) satisfies this criterion.

Determination of the rate of reaction (1) and the profile of the photodissociation lines are left for future study, because we must first improve our detection system to decrease scattering of the signal height of each detection, or to average a large number of data. The three wavelengths of the photodissocation may be assigned to some structure such as vibration or rotation [18]. Search for photodissociation lines of YbH^+ in a wider wavelength region will determine the entire structure and molecular constants.

When rf signals are detected, the resonance point of rf signals shifts toward that of heavier mass in the same time scale of the fluorescence disappearance (this shift is distinguished from a subsequent larger and slower shift due to the reaction with other gases such as O_2 and H_2O gas [8,9]) and move back to the initial resonance point with irradiation at photodissociation wavelengths. This phenomenon was first reported by Bauch *et al.*, who thought that it might be related to Yb^+ ions in the $^2F_{7/2}$ state [7]. According to our present result, however, it is reasonable to interpret this phenomenon as being due to the production and dissociation of YbH^+. In our present setup, we observed the shift of -0.25 V. We estimate the shift of resonance V_{dc} by producing YbH^+ ions. We previously proved that all odd isotopes of Yb^+ are unreactive because their excitation rate is too small owing to optical pumping in the hyperfine structure of the $^2S_{1/2}$ ground state and isotope shift [8,9]. The shift is calculated in the manner described in Ref. [8] to be -0.31 V from the collective oscillation in strong coupling [19] among odd isotopes of Yb^+ and even isotopes of YbH^+. This value is close to the observed shift.

It should be noted that our present results do not deny the possibility of population trapping in the $^2F_{7/2}$ state of Yb^+ in the presence of buffer gases. To support the existence of the population trapping, Gill *et al.* observed that fluorescence of Yb^+ ions in the presence of buffer gas was recovered by irradiation at 3.43 μm, which drove the $^2F_{7/2}$–$^2D_{5/2}$ transition [15]. In ultra-high-vacuum (UHV), existence of the $^2F_{7/2}$ state of Yb^+ itself has been proved by Bell *et al.*, who showed that pumping to the $^2F_{7/2}$ state was made by optically driving to the $^2D_{5/2}$ state and subsequent spontaneous decay to the $^2F_{7/2}$ state, and recovery from the $^2F_{7/2}$ state by driving the $^2F_{7/2}$-$^1[5/2]_{5/2}$ transition at 638 nm [20]. This result was recently reproduced by us in UHV, and we checked with the same experiment used for Fig. 3 that YbH$^+$ was not photodissociated with irradiation at 638 nm. The knowledge obtained in UHV will be useful in further investigations for fully understanding buffer-gas-cooled Yb$^+$.

In view of the establishment of a frequency standard using buffer-gas-cooled Yb$^+$ ions, the production of YbH$^+$ may limit the performance of the frequency standard owing to the difficulty in removing H_2 gas from the vacuum system. To solve this problem, it may be effective to irradiate Yb$^+$ ions simultaneously with radiation to deplete the $^2D_{3/2}$ state or to photodissociate YbH$^+$; however, if the excitation rate of the $^2S_{1/2}$-$^2P_{1/2}$ transition is high enough to populate a number of Yb$^+$ ions in the $^2P_{1/2}$ state stationarily, the YbH$^+$ production may occur even in the $^2P_{1/2}$ state. The production of hydride ions would be observed for other ion species if the energy of the ions, including their kinetic energy, were greater than the threshold energy for their hydride-ion production, especially in the case where the ions have branches to metastable states, as does Yb$^+$, and they were not depleted. If other gases that react with Yb$^+$ in the excited states are present in vacuum, the production of other molecular ions [8,9] is also a problem (we recently confirmed the production of YbO$^+$ by using the mass-selective detection described here); however, except for H_2 gas, the pressure of the reactive gases seems to be able to decrease to a level where the reaction occurs at a negligibly slow rate [8].

Knowledge of the wavelengths of photodissociation lines of molecular ions enables the use of laser-cooled ions in the field of molecular physics and chemistry, because one can keep molecular ions cool by photodissociating them and laser cooling the dissociated atomic ions again. It should also be possible to demonstrate cooled single molecular-ion photodissociation spectroscopy by a frequency sweep of photodissociating radiation, as is the case in single atomic ion spectroscopy [21], where fluorescence on and off states correspond to atomic- and molecular-ion states, respectively. Fluorescence intensity switching of single ions associated with molecular formation and dissociation was reported by Sankey and Madej [22].

V. CONCLUSION

We found that Yb$^+$ in excited states chemically reacts with H_2 gas to form YbH$^+$. YbH$^+$ is photodissociated by irradiation at 369.482, 369.202, and 368.947 nm, which was formerly assigned to the wavelengths for deexcitation of Yb$^+$ in the $^2F_{7/2}$ state to the $^2S_{1/2}$ ground state. One can monitor the production and dissociation of YbH$^+$ via the change in the resonance point of rf signals. The production of YbH$^+$ may be a problem in establishing frequency standards with buffer-gas-cooled Yb$^+$ owing to the difficulty in removing H_2 gas from vacuum systems.

---

[1] See *Proceedings of the 4th Symposium on Frequency Standards and Metrology, Ancona, 1988*, edited by A. DeMarchi (Springer, Berlin, 1989).
[2] L. S. Cutler, R. P. Giffard, and M. D. McGuire, Appl. Phys. B **39**, 251 (1986).
[3] Chr. Tamm, D. Schnier, and A. Bauch, Appl. Phys. B **60**, 19 (1995).
[4] P. T. H. Fisk, M. J. Sellars, M. A. Lawn, and C. Coles, Appl. Phys. B **60**, 519 (1995).
[5] H. Lehmitz, J. Hattendorf-Ledwoch, R. Blatt, and H. Harde, Phys. Rev. Lett. **62**, 2108 (1989).
[6] H. A. Klein, A. S. Bell, G. P. Barwood, and P. Gill, Appl. Phys. B **50**, 13 (1990).
[7] A. Bauch, D. Schnier, and Chr. Tamm, J. Mod. Opt. **39**, 389 (1992).
[8] K. Sugiyama and J. Yoda, IEEE Trans Instrum. Meas. **42**, 467 (1993).
[9] K. Sugiyamaand J. Yoda, Jpn. J. Appl. Phys. **34**, L584 (1995).
[10] K. Sugiyamaand J. Yoda, Hyperfine Interact. **74**, 251 (1992).
[11] J. Yodaand K. Sugiyama, J. Mod. Opt. **39**, 403 (1992).
[12] D. J. Seidel and L. Maleki, Phys. Rev. A **51**, R2699 (1995).
[13] Y. Matsuo, H. Maeda, and M. Takami, Chem. Phys. Lett. **201**, 341 (1993).
[14] Chr. Tamm and D. Schnier, Opt. Commun. **87**, 240 (1992).
[15] A. S. Bell, P. Gill, H. A. Klein, A. P. Levick, and W. R. C. Rowley, J. Mod. Opt. **39**, 381 (1992).
[16] A. A. Radzig and B. M. Smirnov, *Reference Data on Atoms, Molecules, and Ions* (Springer-Verlag, Berlin, 1985).
[17] J. L. Elkind and P. B. Armentrout, J. Phys. Chem. **91**, 2037 (1987); R. Georgiadis and P. B. Armentrout, *ibid.* **92**, 7060 (1988); K. K. Irikura and J. L. Beauchamp, *ibid.* **95**, 8344 (1991).
[18] E.g., C. S. Yeh, K. F. Willey, D. L. Robbins, J. S. Pigrim, and M. A. Duncan, J. Chem. Phys. **98**, 1867 (1993).
[19] K. Jungmann, J. Hoffnagle, R. G. DeVoe, and R. G. Brewer, Phys. Rev. A **36**, 3651 (1987).
[20] P. Gill, H. A. Klein, A. P. Levick, M. Roberts, W. R. C. Rowley, and P. Taylor, Phys. Rev. A **52**, R909 (1995).
[21] J. C. Bergquist, W. M. Itano, and D. J. Wineland, Phys. Rev. A **36**, 428 (1987).
[22] J. D. Sankey and A. A. Madej, Appl. Phys. B **50**, 433 (1990).