Spectroscopic investigation of autoionizing Rydberg states of palladium accessible after odd-mass-selective laser excitation

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Received September 26, 2016; accepted October 27, 2016; published online November 24, 2016

Excitation of the autoionizing Rydberg states of Pd I was initiated by theoretical studies and followed by experimental studies. Due to the spin–orbit interaction, palladium ion Pd II has two electronically ground states, namely 4d⁹(2⁠D₃/₂) and 4d⁹(2⁠D₅/₂), and the former is lower in energy than the latter. We thus expect autoionizing Rydberg states of Pd I between those two ground states of Pd II.

From optical transition selection rules, direct photo-excitation from the ground state of Pd I is expected to give three autoionizing Rydberg series: 4d⁹(2⁠D₃/₂)⁰np[1/2]f, 4d⁹(2⁠D₃/₂)⁰np[3/2]f, and 4d⁹(2⁠D₅/₂)⁰nf[3/2]f designated in the J,K coupling scheme. From photoionization measurements using synchrotron radiation, Karamatskos et al. observed a single autoionizing Rydberg series converging to the 4d⁹(2⁠D₃/₂) state of Pd II. However, the spectral bandwidth of the synchrotron radiation used in the experiment was too large to resolve the three possible Rydberg series. Callender et al. observed high-lying autoionizing Rydberg series by two-photon excitation through the intermediate 4d⁹(2⁠D₅/₂)⁰5p state. Two Rydberg series with quantum defects of ca. 0.0 and 0.5 were observed but no further analysis was presented. Baig et al. measured XUV absorption spectrum of Pd I and observed unresolved autoionizing Rydberg series, 4d⁹(2⁠D₃/₂)⁰np[1/2]f and 4d⁹(2⁠D₃/₂)⁰np[3/2]f (n = 8–17), with quantum defects of ca. 3.0. Recently, Kron et al. reported efficient ionization of Pd II through excitation to autoionizing Rydberg states via three different intermediate states, although the Rydberg series was not fully described and only one autoionizing state with n⁰ = 9 of 4d⁹(2⁠D₃/₂)⁰np or 4d⁹(2⁠D₅/₂)⁰nf was tentatively assigned.

The two-step scheme used in this work for selective excitation of odd-mass isotopes of Pd I using circularly polarized laser pulses followed by a third laser to autoionizing Rydberg states is shown in Fig. 1. As we have reported recently, the two circularly polarized lasers are equivalent to two linearly polarized orthogonally aligned laser pulses, which can reduce technical difficulties. In the present study, we aim to investigate resonant transition to autoionizing Rydberg states via two intermediate states 4d⁹5p(2⁠D₃/₂) and 4d⁹5d(2⁠D₅/₂) by scanning the third laser frequency. For the development of efficient odd-mass isotope separation process, it is of great importance to determine which transition gives the largest ionization yield.
The experimental setup is similar to that used in the previous study. The outputs of three dye lasers (Lambda Physik FL-3002 ×2, Lumonics HD-500) pumped by an excimer laser (Lambda Physik Compex 110) have been used for excitation. Spectral bandwidth is 0.3 cm\(^{-1}\), and two-step selective excitation of odd-mass number isotopes. Excitation to three autoionizing Rydberg series are expected via the 4\(d_9\)\[1\(D_3\)\] intermediate state at 68520.6 cm\(^{-1}\), and 68529.4 cm\(^{-1}\); \(n = 15\), at 70014.3 cm\(^{-1}\), and 70017.4 cm\(^{-1}\); \(n = 16\), at 70127.2 cm\(^{-1}\), and 70129.0 cm\(^{-1}\); \(n = 17\), at 70217.0 cm\(^{-1}\), and 70218.8 cm\(^{-1}\); \(n = 18\), at 70289.4 cm\(^{-1}\), and 70291.0 cm\(^{-1}\). Unidentified peaks exist at: 67675.2 cm\(^{-1}\), 69032.6 cm\(^{-1}\), 69393.1 cm\(^{-1}\), and 69885.3 cm\(^{-1}\).

The result does not follow the general trend of decreasing oscillator strength for increasing \(n\) Rydberg state, as was observed by Karamatskos et al. in which transition to the lowest autoionizing Rydberg state of \(n = 9\) is the most intense. This is because the initial state of the transition is different; in the case of photoionization of Pd I using synchrotron radiation reported by Karamatskos et al., transitions to the autoionizing Rydberg state is from the ground state of Pd I (4\(d^{10}\)), whereas in the present study, the transition is from the 4\(d^5\) state (i.e., after two-step mass-selective excitation). A similar \(n\)-dependence of the transition intensity of Pd I to the result presented here was reported by Ishikawa after three-step excitation to the Rydberg states converging to the lower ground state of Pd II.

Between the two Rydberg series observed, transitions to the Rydberg series I is dominant in signal intensity and they are assigned to 4\(d^5\)\(D_{3/2}\)\(np[1/2]\)\(^\text{I}\) on the basis of both the assignment given by Baig et al. for the principal quantum numbers are given in the spectrum. Rydberg states marked with * indicate those displaying fine-structure splitting: \(n = 10\), at 68520.6 cm\(^{-1}\), and 68529.4 cm\(^{-1}\); \(n = 15\), at 70014.3 cm\(^{-1}\), and 70017.4 cm\(^{-1}\); \(n = 16\), at 70127.2 cm\(^{-1}\), and 70129.0 cm\(^{-1}\); \(n = 17\), at 70217.0 cm\(^{-1}\), and 70218.8 cm\(^{-1}\); \(n = 18\), at 70289.4 cm\(^{-1}\), and 70291.0 cm\(^{-1}\). Unidentified peaks exist at: 67675.2 cm\(^{-1}\), 69032.6 cm\(^{-1}\), 69393.1 cm\(^{-1}\), and 69885.3 cm\(^{-1}\).

The state energies of the Rydberg states \(E(n)\) can be described approximately by the extended Ritz formula as

\[
E(n) = \frac{1}{2} \left( \frac{\omega_1}{\omega_3} \right)^2 n^2 - \frac{1}{2} \left( \frac{\omega_1}{\omega_3} \right)n + \omega_3.
\]
Table I. Energy, effective quantum number \((n^*)\) and relative ion yield of the transitions to autoionizing Rydberg states observed in the present study. The yield is normalized to the value for 4d\(^9\)(D\(_{3/2}\))11p[1/2]\(^{2}\)\(^{0}\). \(E(n) = \text{IP} - \frac{R_{pd}}{[n - \delta(n)]^2}\) \(\text{(1)}\)

\[
\delta(n) = \delta_0 + \frac{\delta_2}{(n - \delta_0)^2}, \quad \text{\(\text{(2)}\)}
\]

where IP is the ionization energy of Pd I, \(R_{pd}\) is the mass-corrected Rydberg constant of Pd I \((109736.75 \text{ cm}^{-1})\), and both \(\delta_0\) and \(\delta_2\) are the energy-dependent quantum defects. By least squares fitting using \(\delta_0\) and \(\delta_2\) as fitting parameters, we have obtained IP of 70780.38 ± 0.08 cm\(^{-1}\) with \(\delta_0 = 3.0255 \pm 0.0013\) and \(\delta_2 = -0.0339 \pm 0.051\). The IP obtained here has a lower uncertainty and is within the range of values reported in literature \((70780 \pm 1\) and \(70779.8 \pm 0.8 \text{ cm}^{-1})\).\(^{15,17}\)

The assignment of Rydberg series I and II to 4d\(^9\)(D\(_{3/2}\))np[1/2]\(^{0}\)\(^{0}\) and 4d\(^9\)(D\(_{3/2}\))np[3/2]\(^{0}\)\(^{0}\), respectively, is based on the energies reported for the lower states, \(n = 5\) and \(6\).\(^{20}\) We observe fine-structure splitting of levels \(n = 10, 15, 16, 17,\) and \(18\); possibly due to the presence of a local perturbation. However, no definite candidate of the perturbing state can be presented here because of the lack of spectroscopic data on the two-electron excited states in this energy region.\(^{22}\)

From transition rules, we also expect 4d\(^9\)(D\(_{3/2}\))np[3/2]\(^{0}\)\(^{0}\), however, we do not observe any members of this series. Similarly, this series was not observed in other studies, possibly due to low signal intensity.\(^{14,17}\)

Of the two observed Rydberg series converging to the upper ionization limit of palladium after odd-mass number selective excitation, resonant excitation to the 4d\(^9\)(D\(_{3/2}\))11p[1/2]\(^{2}\)\(^{0}\) state gives the largest ion yield. This result is a significant aid in the development of an efficient separation process of the LLFP of palladium \(^{10}\)Pd from nuclear waste.

As we have specified, this study was carried out on the basis of the selective excitation scheme for odd-mass number isotopes of palladium proposed by Chen.\(^9\) However, during our investigation another mass selective excitation scheme was found utilizing intermediate states of Pd I with a 6d\(^9\)(D\(_{3/2}\)) ion core, showing a significantly increased efficiency of ionization via autoionizing Rydberg states. Results using this new selective excitation scheme will be reported in the near future.

Acknowledgment This work was funded by ImPACT Program of Council for Science, Technology and Innovation (Cabinet Office, Government of Japan).

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