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Reassessment of the first ionization potentials of copper, silver, and gold

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The first ionization potentials (V_{IP}'s) of copper, silver, and gold have been reassessed using a two-color resonant excitation scheme on laser-vaporized atomic beams of Cu, Ag, and Au. Rydberg levels of the $nd^{10}n_Rs^1(^2S_{1/2})$ and $nd^{10}n_Rd^1(^2D_{3/2,5/2})$ series converging to the ground ^1S term of the singly charged cations were excited and pulse-field ionized. The fit to the Rydberg levels yielded the ionization potentials $V_{\mathrm{IP}}(\mathrm{Cu}) = 62\,317.3(2)$ cm^{-1}, $V_{\mathrm{IP}}(\mathrm{Ag}) = 61\,106.45(20)$ cm^{-1}, and $V_{\mathrm{IP}}(\mathrm{Au}) = 74\,409.0(2)$ cm^{-1}. A comparison of these results to the currently accepted values revealed slight discrepancies to the previously reported IP of silver. [S1050-2947(99)09901-1]

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Ionization potentials (V_{IP}'s) of atoms and molecules are fundamental quantities of great importance in many areas of physics and chemistry. They provide crucial information of the electronic structure and, therefore, are often used as benchmarks for theoretical methods [1]. Also when used in the appropriate thermodynamic cycles, V_{IP}'s relate to bond strengths. In the simplest case, when bond energies of diatomic molecules are sought, the first V_{IP}'s of atoms are required. The currently accepted values of $V_{\mathrm{IP}}(\mathrm{Cu}) = 62\,317.44(10)$ cm^{-1}, $V_{\mathrm{IP}}(\mathrm{Ag}) = 61\,104.30(6)$ cm^{-1}, and $V_{\mathrm{IP}}(\mathrm{Au}) = 74\,408.88(17)$ cm^{-1} deviate only in the case of silver considerably from the still commonly used values recommended by Moore [2], $V_{\mathrm{IP}}(\mathrm{Cu}) = 62\,317.2$ cm^{-1}, $V_{\mathrm{IP}}(\mathrm{Ag}) = 61\,106.50$ cm^{-1}, and $V_{\mathrm{IP}}(\mathrm{Au}) = 74\,410.0$ cm^{-1}.

The most recent value for the ionization potential of Copper is given by Sugar and Musgrove [3] in their compilation of spectral lines, which were previously recorded by Longmire *et al.* [4] and by Tondello [5]. The value quoted by Moore, on the other hand, is derived from a Rydberg spectrum published by Shenstone [6].

The ionization potential of silver was measured by Ishikawa [7] in his study of the high-n Rydberg states of this atom, whereas the value quoted by Moore is again derived from an arc spectrum recorded by Shenstone [8]. The discrepancy of 2.20 cm^{-1} in the V_{IP}'s reported by Ishikawa and by Moore is troubling and raises some questions about the reliability of the IP's measured through fits to low members of the Rydberg series. It is this discrepancy that prompted this study.

Finally, the most recent value for the V_{IP}'s of gold was obtained by Brown and Ginter [9] using absorption spectroscopy in a King furnace. The value quoted in Moore's com-

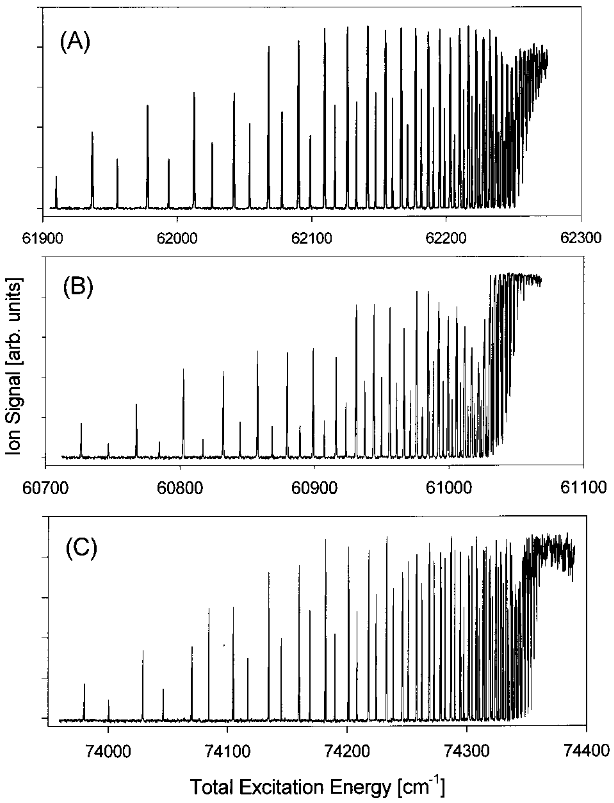

FIG. 1. Rydberg spectra of (a) copper, (b) silver, and (c) gold. From the $nd^{10}(n+1)p^1$ intermediate state the allowed Rydberg series are of the type $nd^{10}n_Rs^1(^2S_{1/2})$ and $n^{10}n_Rd^1(^2D_{3/2,5/2})$. The lines of the $nd^{10}n_Rs^1(^2S_{1/2})$ series in all spectra have slightly lower intensities than the $nd^{10}n_Rd^1(^2D_{3/2,5/2})$ series.

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TABLE I. Ionization potentials (IP) and quantum defects (δ) of copper, silver, and gold (in cm^{-1}). The V_{IP}'s and quantum defects were determined from the fit of the spectra to the Rydberg equation with 2σ standard deviation quoted in parentheses. The uncertainties of the recommended V_{IP}'s are determined by the laser linewidth.

	Cu		Ag		Au	
	$3d^{10}ns^1$	$3d^{10}nd^1$	$4d^{10}ns^1$	$4d^{10}nd^1$	$5d^{10}ns^1$	$5d^{10}nd^1$
n range	19–46	18–49	21–46	19–42	21–48	19–44
IP fit	62 317.29(3)	62 317.32(3)	61 106.37(4)	61 106.52(5)	74 409.02(5)	74 408.95(7)
δ fit	2.584(2)	1.018(2)	3.530(3)	2.006(3)	4.641(2)	3.007(3)
IP (this work)	62 317.3(2)		61 106.45(20)		74 409.0(2)	
IP (literature)	62 317.44(10) [3]		61 104.30(6) [7]		74 408.88(17) [9]	
	62 317.2 [6]		61 106.50 [8]		74 410.0 [10]	

pilation is derived from spectra recorded by Platt and Sawyer [10].

In this Brief Report, we intend to reassess the values for the first ionization potentials and to provide a brief critique of earlier measurements. The ionization potentials were determined by recording Rydberg series that converge to the lowest electronic term of the ion. Using a well-defined intermediate state in a two-color pumping scheme greatly simplifies the spectra.

The experimental setup has been described before [11] and only details relevant to this set of experiments will be addressed. A Smalley-type ablation source is used to prepare the coinage metal sample in an atomic beam. The output of a tunable Nd:YAG laser pumped dye laser was used to excite the atoms to the intermediate state. These intermediate terms were assigned using Refs. [12] and [13] and were $3d^{10}4p(^2P_{1/2})$ for Cu at 30 535.302 cm^{-1}, $4d^{10}5p(^2P_{1/2})$ for Ag at 29 552.05 cm^{-1}, and $5d^{10}6p(^2P_{1/2})$ for Au at 37 358.991 cm^{-1}. The frequency-doubled output of a second excimer-pumped dye laser is used to excite the Rydberg states 10–20 ns after excitation to the intermediate state. These Rydberg states were pulsed-field ionized in the first stage of a Wiley-McLaren time-of-flight mass spectrometer (TOF-MS) by a delayed ($\Delta t = 5\ \mu$s) electric field (typically 500 V). The ions were then detected using z-stacked microchannel plates and the signal was subsequently digitized and processed by a personal computer. Calibration of the spectra to an accuracy of the laser linewidth ($\Delta\omega = 0.15\ \mathrm{cm}^{-1}$) was conducted using the reported lines [14] of a Fe-Ne hollow cathode lamp.

Rydberg series recorded in this way are presented in Fig. 1. Since for all metals the intermediate state was of the type $nd^{10}(n+1)p^1$, the allowed Rydberg series will be of the type $nd^{10}n_Rs^1(^2S_{1/2})$ and $nd^{10}n_Rd^1(^2D_{3/2,5/2})$. These series converge to the ground ^1S term of the singly charged ion. They were assigned to the main quantum numbers n using reported line positions for Cu [3] and extrapolation of the respective series for Ag and Au [12]. Comparison with the Cu $3d^{10}ns^1(^2S_{1/2})$ line positions reported by Sugar and Musgrove [3] shows that our data lie within 0.15 cm^{-1} of their values.

The two observed series were fitted to

$$E_n = V_{\mathrm{IP}} - \frac{R}{(n-\delta)^2},$$

where E_n is the energy of the nth Rydberg level, V_{IP} is the convergence limit, δ is the quantum defect for the series, and R is the Rydberg constant for the considereed coinage atom. For all three atomic species, we were able to observe for a number of lines a splitting of the ^2D levels into the two spin-orbit components. However, since the splitting at these high n-quantum numbers was smaller or on the order of the laser linewidth, the center of the doublets was used for the fit. For the coinage metal atoms, the simple Rydberg formula gives a good approximation of the quantum defect and ionization potential, since the ion core has a closed electronic shell. Furthermore, the quantum defect in this range of n is constant as has been shown in previous studies on Pt [15], Os, Ir [16], W, and Re [17]. The series were fitted to the above expression using a standard nonlinear least-squares procedure in which the IP and the quantum defect, δ, were the adjustable parameters. The results of the fits are listed in Table I.

The error quoted in Table I refers to the 2σ standard deviation of the fit. However, the actual error in the experiments is determined by the laser linewidth of ~0.3 cm^{-1} FWHM and the uncertainty in the calibration (0.2 cm^{-1}). We therefore recommend the ionization potentials $V_{\mathrm{IP}}(\mathrm{Cu}) = 62\,317.3(2)\ \mathrm{cm}^{-1}$ [7.726 36(6) eV], $V_{\mathrm{IP}}(\mathrm{Ag}) = 61\,106.45(20)\ \mathrm{cm}^{-1}$ [7.576 24(2) eV], and $V_{\mathrm{IP}}(\mathrm{Au}) = 74\,409.0(2)\ \mathrm{cm}^{-1}$ [9.225 54(2) eV]. These values compare very well with the literature values for the V_{IP}'s except in the case of silver, where we find very good agreement with the value determined from Shenstone's [8] spectrum and quoted by Moore [2] [$V_{\mathrm{IP}}(\mathrm{Ag}) = 61\,106.50\ \mathrm{cm}^{-1}$], but not with the value given by Ishikawa [7] of $V_{\mathrm{IP}}(\mathrm{Ag}) = 61\,104.30(6)\ \mathrm{cm}^{-1}$. The reason for this discrepancy is unknown. We note, however, that of the two series, on which Ishikawa reported, only the $4d^{10}np^1(^2P_{1/2})$ series converges to 61 104.30(5) cm^{-1}, whereas the shorter $4d^{10}nf^1(^2F_{1/2})$ series converges to 61 105.4(5) cm^{-1}. Also, it is possible that the accuracy of Ishikawa's data is not determined by the standard deviation of the least-squares fitting procedure as was assumed, but by the uncertainty in the calibration of the lasers caused by the considerable linewidth of 1 cm^{-1} (quoted by Ishikawa) to 8 cm^{-1} (estimated from Fig. 1 in Ref. [7]) full width at half maximum.

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[1] P. Neogrady, V. Kellö, M. Urban, and A. J. Sadlej, Int. J. Quantum Chem. **63**, 557 (1997).
[2] C. E. Moore, *Ionization Potentials and Ionization Units Derived from the Analyses of Optical Spectra*, Natl. Bur. Stand. (U.S.) Circ. No. NSRDS-NBS 34 (U.S. GPO, Washington, D.C., 1970).
[3] J. Sugar and A. Musgrove, J. Phys. Chem. Ref. Data **16**, 527 (1990).
[4] M. S. Longmire, C. M. Brown, and M. L. Ginter, J. Opt. Soc. Am. **70**, 423 (1980).
[5] G. Tondello, J. Opt. Soc. Am. **63**, 346 (1973).
[6] A. G. Shenstone, Philos. Trans. R. Soc. London, Ser. A **241**, 832 (1948).
[7] T. Ishikawa, Jpn. J. Appl. Phys., Part 1 **33**, 2056 (1994).
[8] A. G. Shenstone, Phys. Rev. **57**, 894 (1940).
[9] C. M. Brown and M. L. Ginter, J. Opt. Soc. Am. B **68**, 243 (1978).
[10] J. R. Platt and R. A. Sawyer, Phys. Rev. **60**, 866 (1941).
[11] A. M. James, P. Kowalczyk, E. Langlois, M. D. Campbell, A. Ogawa, and B. Simard, J. Chem. Phys. **101**, 4485 (1994).
[12] C. E. Moore, *Ionization Potentials and Ionization Units Derived from the Analysis of Optical Spectra*, Nat'l. Bur. Stand. (U.S.) Circ. No. NSRDS-NBS 35 (U.S. GPO, Washington, D.C., 1971).
[13] J. C. Ehrhardt and S. P. Davis, J. Opt. Soc. Am. **61**, 1342 (1971).
[14] H. M. Crosswhite, *Crosswhite's Fe-Ne Hollow Cathode Tables* (Johns Hopkins University, Baltimore, MD, 1965).
[15] A. Marijnissen, J. J. ter Meulen, P. A. Hackett, and B. Simard, Phys. Rev. A **52**, 2606 (1995).
[16] P. Colarusso, M.-A. Lebeault-Dorget, and B. Simard, Phys. Rev. A **55**, 1526 (1997).
[17] M. D. Campbell-Miller and B. Simard, J. Opt. Soc. Am. B **13**, 2115 (1996).