Symmetric charge-transfer cross sections of III*a* rare-earth-metal elements

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Symmetric charge-transfer cross sections of III*a* rare-earth-metal elements (Sc, Y, and Gd) in the impact energy range of 30 to 1000 eV were measured for the first time. The experiments were performed with a crossed-beam apparatus that featured primary ion production by photoionization with a tunable dye laser. Comparing the cross sections of III*a* rare-earth-metal elements (σ_{Sc}, σ_Y, and σ_{Gd}) with those of alkali metals or helium σ_0, we found that $\sigma_0 \approx \sigma_{Sc} < \sigma_Y < \sigma_{Gd} \approx 2\sigma_0$at an impact energy of 1000 eV.

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I. INTRODUCTION

Symmetric charge-transfer processes have been investigated since the 1930s. However, the elements studied have been limited mainly to hydrogen, alkali metals, and noble gases [1–5]. Being motivated by the significant lack of data [6] about the charge-transfer cross sections for transition metallic elements, we developed a new crossed-beam apparatus [7,8], with which the cross section of gadolinium was successfully measured [9,10]. An anomalously large cross section was obtained for Gd [10]. The possibility that this result is due to the unreliability of measurements made using the apparatus has been ruled out by comparing experiments on $Ca + Ca^+$ with other published data [11,12]. So the large cross section for Gd has not yet been clearly understood and needs further investigation. We are, therefore, studying the cross sections of rare-earth-metal elements systematically. In this paper we report the measurement of the cross sections for Sc and Y, and we compare the results with the Gd data acquired previously.

II. EXPERIMENTS

The experimental technique has been reported in detail in previous papers [7–9] and is only described briefly here. The crossed-beam apparatus features laser photoionization to produce primary ions in an atomic beam. Two atomic beams were produced by collimating atomic vapor emitted from a crucible filled with the objective metal, which was heated with an electron-beam gun. One of the atomic beams was partially photoionized by light from a pulsed dye laser, and the primary ions produced were extracted from the atomic beam and accelerated by a static electric field applied in the laser-atom interaction region. The primary ions were detected by an ion collector plate after colliding with another atomic beam. The collision energy was varied from 30 to 1000 eV by controlling the strength of the electric field. The secondary ions produced by the charge-transfer collisions stream upward as fast as the atoms in the beam. These were focused by an ion lens and guided toward a ceramic electron multiplier detector located above the ion-atom interaction region. Table I summarizes the experimental condition for producing atomic and ion beams. The internal energy population in atomic beams is calculated with the assumption of thermal equilibrium in the crucible. The populations of Gd atoms and primary ions before collisions have been measured separately by the laser-induced fluorescence method [13]. The measured population of Gd atoms can be reasonably explained by thermal equilibrium [10], while the population of primary ions depends on the wavelength of the laser used for photoionization. Y and Sc atoms are also considered to be thermally populated, corresponding to the source temperature on the surface of the metal source in the crucible. Figure 1 shows the photoionization schemes for the rare-earth-metal elements Sc, Y, and Gd in the present experiment. The laser wavelength was tuned so that the primary ions produced in the atomic beam were intense enough to measure the cross sections with the crossed-beam apparatus. It was found that the atoms were photoionized efficiently by a two-photon resonance. For Y and Gd atoms, the two-photon resonance is not reached from the ground state but from the first excited state. The ions produced populate the ground state and the excited states with internal energy less than $3\epsilon + E_0 - I$, where ϵ is the photon energy, E_0 is initial atomic internal energy, and I is the ionization potential of an atom of the element.

III. RESULTS AND DISCUSSION

Figure 2 shows the cross sections for charge transfer between an atom of Sc, Y, or Gd and the corresponding singly charged positive ion. The cross section at each impact energy was obtained by averaging 1024 data points using a fast data acquisition system [8]. The uncertainties in the cross sections measured with the present apparatus were <6.8% and <8.1% for impact energies of >40 eV and <40 eV, respectively. These uncertainties are due to a combination of the fluctuation of the atomic density (<1.8% and <3.1%, respectively) and the accuracy of the detector calibration (5%). To discuss the cross sections obtained experimentally, universal formulas are available that can be used. The derivation of theoretical or semiempirical formulas has been studied, for example,

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TABLE I. Characteristics of primary atomic and ion beams.

	Atomic beam			Ion beam			
Elements	Source temperature in crucible (K)	Populated states (cm^{-1})	Population (%)	Ionization potential I (cm^{-1})	Wavelength of laser for photoionization ϵ (nm)	Transition for two-photon resonance (cm^{-1})	$3\epsilon+E_0-I$[a] (cm^{-1})
$_{21}$Sc	1640	168	56.6	52920	560.680	$0 \rightarrow 35671$	587
		0	43.4				
$_{39}$Y	1930	530	50.2	52650	557.092	$530 \rightarrow 36431$	1731
		0	49.8				
$_{64}$Gd	2000	1719	14.4	49603	606.425	$215 \rightarrow 33195$	82
		999	20.4				
		533	23.3				
		215	22.8				
		0	19.0				

[a]ϵ is the photon energy of the laser to produce primary ions, E_0 is the energy of the initial level for photoionization, and I is the photoionization potential of an elemental atom.

by Müller *et al*. [14] and Selberg *et al*. [15] for highly charged ion-atom collisions. Here, for the consideration of singly charged ion-atom collisions, we use the simple formula proposed by Sakabe *et al*. [16], which was derived from both numerical calculation and accumulated experimental data on symmetric (resonant) charge transfer. They compiled all the experimental data from resonant charge-transfer measurements and found a simple formula that fit the data well. The formula is a function only of the impact velocity v (cm/s) and the ionization potential I (eV) of the element:

$$\sigma(v) = (A - B\log_{10} v)(I/I_0)^{-1.5}\,(\mathrm{cm}^2), \tag{1}$$

where $A = 1.81 \times 10^{-14}$ cm^2, $B = 2.12 \times 10^{-15}$ cm^2, and $I_0 = 13.6$ eV. For the nonresonant process, we used the calculation done by Rapp and Francis [17], which we modified in our previous work [10]. The Sakabe formula shows that the cross section can be related to the ionization potential I by $\sigma \propto (I/I_0)^{-1.5}$, while the calculation by Rapp and Francis yields the relation $\sigma \propto I^{-1}$. This disagreement is mainly due to the probability of the charge transfer being calculated with the one-electron wave function in Rapp and Francis' approach. For discussion of the physics of charge-transfer collisions, how far the wave function is tailed is highly important. For elements with a complex electron configuration, the tail of the wave function cannot be precisely expressed by a one-electron wave function. In order to achieve a better fit between calculation results and experimental data, the wave function used by Rapp and Francis was modified as follows [10]:

$$\Psi(r) = (\pi a_0^3)^{-1/2}\left(\frac{I}{I_0}\right)^{9/8}\exp\left[-\left(\frac{I}{I_0}\right)^{3/4}\frac{r}{a_0}\right],$$

It can be seen that the cross sections measured at low impact energy are close to the values predicted by the formula, while, as impact energy increases up to 1000 eV, the cross sections become larger than predicted. The cross sections of Sc, Y, and Gd (σ_{Sc}, σ_{Y}, and σ_{Gd}, respectively) show the pattern $\sigma_0 \approx \sigma_{\mathrm{Sc}} < \sigma_Y < \sigma_{\mathrm{Gd}} \approx 2\sigma_0$ at an impact energy of 1000 eV, where σ_0 is given by the Sakabe formula (1). The results of our work suggest that the impact energy dependence of cross sections can be explained by assuming that the process includes both resonant and nonresonant parts:

$$\sigma = \eta\sigma^{\mathrm{R}} + (1-\eta)\sigma^{\mathrm{NR}}, \tag{2}$$

where η is the fraction of the resonant process and σ^{R} and σ^{NR} are the resonant and nonresonant charge-transfer cross

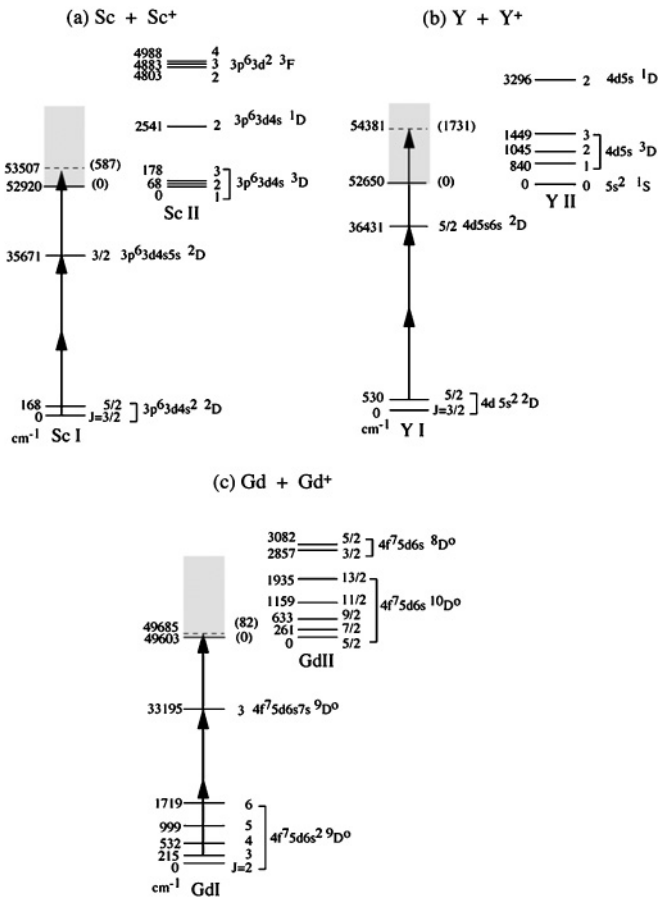

FIG. 1. Three-photon ionization transition via a two-photon resonance for Sc, Y, and Gd.

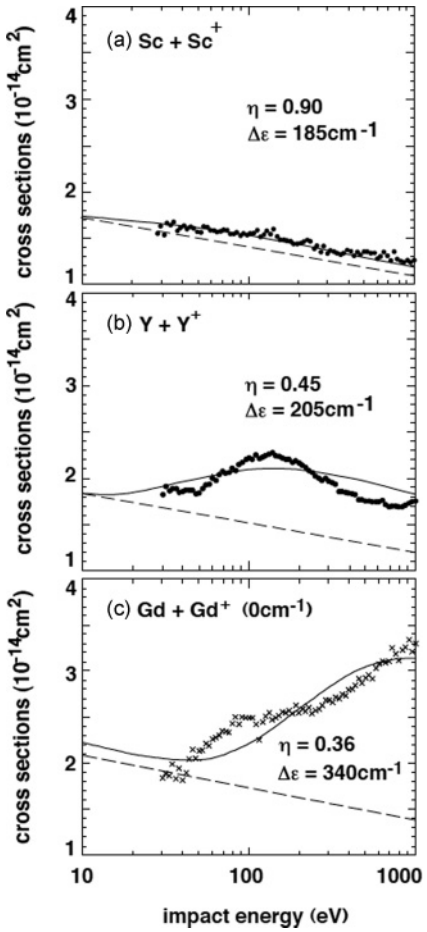

FIG. 2. Dependence of the symmetric charge-transfer cross section on impact energy for Sc, Y, and Gd. The symbols are the data from our experiments. The dashed line is Sakabe's formula for symmetric charge transfer [16]. The solid lines show the results of a calculation with the assumption that the process includes resonant and nonresonant parts. The values of $\Delta\epsilon$ for the nonresonant process and η for the rate of the resonant process were adjusted to provide a good fit between the calculation and the experimental data.

sections, respectively. The cross sections are calculated under the assumption that the fraction η is constant. The fraction may not be varied with the impact energy because the populations of the atoms and ions do not depend on the impact energy. The cross sections σ^R and σ^{NR} are given by Sakabe's formula and the modified Rapp and Francis calculation [10], respectively. The absolute values of σ^R and σ^{NR} are multiplied to fit the experimental data at 1000 eV, giving the solid lines in Fig. 2. The best fits of the calculated impact-energy dependence with the experimental data are obtained for $\eta = 0.90$, 0.45, and 0.36 and $\Delta\epsilon = 185$, 205, and 340 cm^{-1} for Sc, Y, and Gd, respectively. Here $\Delta\epsilon$ is the internal energy difference between the initial state and the final state for the nonresonant charge-transfer process. The impact energy dependence can be qualitatively explained by the model in Eq. (2). It can also be seen that as the principle quantum number of the outer electron becomes smaller, the fraction of the resonant process tends to become larger. A significant defect in this simple model is discussed below. Atoms and ions have some metastable excited states near the ground state, and the charge-transfer process between an atom A and its ion A^+ can be represented by the formula

$$A(i) + A^+(j) \rightarrow AA^+ \rightarrow A^+(k) + A(l),$$

where i indicates an internal energy of i cm^{-1} and $i = 0$ corresponds to the ground state. With the cross section of the process above being σ_{ijkl}, the total cross section of the charge transfer σ may be written as

$$\sigma = \sum_{ijkl} g_{ijkl}\sigma_{ijkl}, \tag{3}$$

where g_{ijkl} is the statistical degeneracy of each process and $g_{ijkl} \leqslant 1$. For elements without metastable states near the ground state, the charge-transfer cross section has been studied theoretically with a two-state model: that is, the atom is modeled as having only the ground state and the ionization state. This model has been used to calculate the cross section for the nonresonant process $A + B^+ \rightarrow A^+ + B$, and the charge-transfer cross sections for hydrogen, alkali metals, and rare gases have been well explained. If each process is independent, then each σ_{ijkl} can be simply calculated in this way, and the total cross section is given by the linear summation in Eq. (3). Under this assumption, σ should be less than σ_{ijkl}, where σ_{ijkl} is the resonant charge-transfer cross section for $(k-j)^2 + (l-i)^2 = 0$ and is the nonresonant charge-transfer cross section for $(k-j)^2 + (l-i)^2 \neq 0$. The calculations may be carried out, for example, using Sakabe's formula for the resonant cross section $\sigma^{\mathrm{R}}_{ijkl}$ and the Rapp and Francis [17] method for the nonresonant cross section $\sigma^{\mathrm{NR}}_{ijkl}$. However, with a two-state model, $\sigma^{\mathrm{NR}}_{ijkl}$ should be less than or equal to $\sigma^{\mathrm{R}}_{ijkl}$, regardless of which method is used for the calculation. Therefore, σ should never be larger than σ_0. However, our experimental results show $\sigma > \sigma_0$, which suggests that the cross section is too large to be explained by the long interaction distance between two nuclei, that is, by the tail length of the atomic wave function of the electron to be transferred. We conjecture that the total cross section is not a simple linear summation of each process cross section and that the interactions between the many metastable states of atoms and ions are more complex. For elements with many metastable states, such as the present case, it is not at all certain that such a simple two-state model is applicable to the prediction of cross sections, and it should be studied theoretically in much more detail in the future.

IV. CONCLUSION

The charge-transfer cross sections for the III*a* rare-earth-metal elements Sc, Y, and Gd have been measured successfully for an impact energy range of 30–1000 eV, and some significant features have been found. These features are never seen in the cross sections for well-studied elements, such as hydrogen, alkali metals, and helium. We can explain the impact energy dependence by a simple two-state model that includes both resonant and nonresonant processes; however, the absolute value of the charge-transfer cross sections cannot be explained using this model. We hope that these observations will stimulate the study of the physics of collisions between elements with complex electron configurations.

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