Experimental Link of Photoionization of Sc^{2+} to Photorecombination of Sc^{3+}: An Application of Detailed Balance in a Unique Atomic System

S. Schippers,[1] A. Müller,[1] S. Ricz,[2] M. E. Bannister,[3] G. H. Dunn,[4] J. Bozek,[5] A. S. Schlachter,[5] G. Hinojosa,[6] C. Cisneros,[6] A. Aguilar,[7] A. M. Covington,[7] M. F. Gharaibeh,[7] and R. A. Phaneuf[7]

[1]*Institut für Kernphysik, Justus-Liebig-Universität, 35392 Giessen, Germany*
[2]*Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), H-4001 Debrecen, Hungary*
[3]*Physics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831*
[4]*JILA, University of Colorado, Boulder, Colorado 80309-0440*
[5]*Advanced Light Source, Lawrence Berkeley Laboratory, Berkeley, California*
[6]*Centro de Ciencias Fisicas, Universidad Nacional Autonoma de Mexico, Apartado Postal 6-96, Cuernavaca 62131, Mexico*
[7]*Department of Physics, University of Nevada, Reno, Nevada 89557*

(Received 21 June 2002; published 18 October 2002)

The principle of microscopic time reversal of physical processes, detailed balance, is widely used and depended upon in the theoretical community as a connection between photorecombination (PR) and photoionization (PI). This paper reports on a novel use of detailed balance and the comparison of experimental results obtained by two very distinct techniques to determine both the metastable fraction of an ion beam and partial Sc^{3+} PR cross sections and partial Sc^{2+} PI cross sections for the ground state and for two metastable states. The Sc^{2+} to Sc^{3+} system presents a unique opportunity to obtain comprehensive state-selective information by combining results from PR and PI experiments.

DOI: 10.1103/PhysRevLett.89.193002 PACS numbers: 32.80.Fb, 32.80.Hd, 34.80.Lx

The principle of detailed balance is widely used in the theoretical description of microscopic processes, as has been experimentally demonstrated in nuclear reactions (see, e.g., Ref. [1]). The intimate connection through detailed balance of photoionization (PI) and photorecombination (PR) is heavily relied upon for the description of hot plasma environments, such as those encountered in astrophysics, controlled fusion, and explosions. An international consortium has for some years been calculating relevant PI cross sections, and detailed balance is used to provide PR cross sections [2]. The atomic ions Sc^{2+} and Sc^{3+} provide a unique opportunity to directly observe this widely applied principle between PI of the former and PR of the latter due to the exceptional strength of the $3d \rightarrow 3p$ radiative decay of $3p^5 3d^2$ and $3p^5 3d 4s$ PR resonances. By combining the high resolving power of a PI experiment at a synchrotron light source with the state selectivity of a heavy-ion storage-ring PR experiment we are able to derive comprehensive state-selective information about the atomic system under study on a purely experimental basis.

With the advent of powerful synchrotron light sources it has become feasible to conduct PI measurements using low-density ion beams as targets [3–9] and to benchmark theoretical calculations. A complication which is not easily overcome, is the existence of usually unknown fractions of metastable states in the ion beams used in these experiments. Metastable states are populated in ion sources, where ions are formed by electron bombardment in a hot plasma. If the metastable states are sufficiently long lived, they will survive the transport from the ion source to the PI measurement region and therefore contribute to the measured PI signal. Accordingly, the derivation of absolute cross sections from PI measurements requires knowledge of the ion-beam composition. This knowledge, however, is usually not available. The ion-beam composition is either completely unknown [4], or rough estimates, based on the assumption that the population of the various states follows statistical rules, are used [5], or the metastable fractions are inferred from a comparison with theoretical predictions for the PI cross sections [7,8]. In all these cases, a considerable level of ambiguity is introduced in the determination of absolute cross sections.

In some cases it is possible to determine the ion-beam composition from charge-transfer measurements in a gas cell [6]. This method, however, does not give access to the population of fine-structure components or to the relative population of states that are otherwise energetically too close to each other. The same limitations apply for state preparation by translational-energy spectroscopy [10]. For the relative population of closely spaced fine-structure levels (that often remain experimentally unresolved) the assumption of a statistical distribution is commonly believed to be quite adequate. Here we present an example of a significant deviation from the statistical population of fine-structure levels.

Our method to determine the fine-structure composition of the ion beam is to compare our measured Sc^{2+} PI cross sections with the experimental Sc^{3+} PR cross section of Schippers *et al.* [11] thereby exploiting the fact that PI and PR are linked on a state to state level by the principle of detailed balance. Accordingly, the cross section $\sigma^{(PI)}_{i\rightarrow f}$ for PI from an initial state i to a final state f can be used [12] to calculate the cross section $\sigma^{(\mathrm{PR})}_{f\to i}$ for the time inverse PR process, i.e.,

$$\sigma^{(\mathrm{PR})}_{f\to i}(E_{\mathrm{cm}}) = \frac{(h\nu)^2}{2m_e c^2\, E_{\mathrm{cm}}} \frac{g_i}{g_f}\, \sigma^{(\mathrm{PI})}_{i\to f}(h\nu), \qquad (1)$$

with the statistical weights g_i and g_f. The photon energy $h\nu$ and the energy E_{cm} of the free electron in the electron-ion center-of-mass frame are related by $h\nu = E_{\mathrm{cm}} + I_i$ with the ionization energy I_i of state i.

We employed the merged photon-ion-beams method [3] to record PI cross sections. The experiment was performed at the photon-ion-end-station [6] of the undulator beam line 10.0.1 of the Advanced Light Source. The Sc^{2+} ion beam was generated by ionizing scandium atomic vapor by electron bombardment inside a compact electron cyclotron resonance (ECR) source. A dipole magnet was used to select the desired charge-to-mass ratio. Downstream from the interaction zone the ion beam was deflected out of the photon beam direction by a second dipole magnet that also separated the ionized Sc^{3+} product ions from the Sc^{2+} parent ions. The Sc^{3+} ions were counted with nearly 100% efficiency with a single-particle detector. The relative PI cross section is derived from the measured Sc^{3+} count rate by normalization to both photon flux and ion current.

In principle, the cross section can be put on an absolute scale by measuring the mutual overlap of the ion and the photon beams. In our experimental setup this is usually achieved with a movable slit in the center of the voltage labeled interaction region and with two wire scanners at each end of the interaction zone [6]. However, at the time of this experiment the rather low ion currents of typically 4 nA prohibited the use of the wire scanners for a reliable beam overlap measurement. Therefore, in this work the absolute Sc^{2+} cross section has been determined by applying the principle of detailed balance, i.e., by comparison with the measured absolute Sc^{3+} PR cross section from a storage-ring experiment [11] (see below).

Our Sc^{2+} cross section in the region of the $3p^5 3d^2$ and $3p^5 3d\,4s$ resonances is shown in Fig. 1 together with the only available theoretical result [13]. Apart from the shape of the broad $3d^2\,(^3F)\,^2F$ resonance the theory obviously does not reproduce the measurement very well. There are two reasons for this discrepancy. First, in the theoretical treatment relativistic effects, i.e., fine-structure splittings, were neglected entirely and correlation was treated only approximately. Second, in the experiment besides PI of $Sc^{2+}(3p^6 3d)$ ground-state ions also PI of metastable $Sc^{2+}(3p^6 4s)$ ions occurred. The latter was not accounted for in the calculations. The theoretical result can therefore not be used for the identification of the measured resonance features. We have identified [14] some of the resonances with the aid of atomic structure calculations using the codes of Cowan [15]. Next to resonances excited from the $Sc^{2+}(3p^6 3d\ ^2D_{3/2})$ ground state there are also strong resonances excited from the $3p^6 3d\ ^2D_{5/2}$ and $3p^6 4s\ ^2S_{1/2}$ metastable states. Contributions from direct ionization are insignificant and are disregarded in the present context. In order to put the measured cross section on an absolute scale the ground state and metastable state fractions in the ion beam have to be determined. In the following this will be achieved on a purely experimental basis by comparing the measured Sc^{2+} PI cross section with the measured Sc^{3+} PR cross section via the principle of detailed balance [Eq. (1)].

One has to be aware of the fact that the number of PR channels starting from state f is much larger than the number of PI channels ending in state f (Fig. 2). Total PR cross sections, such as usually measured in merged-beams electron-ion recombination experiments, therefore cannot be directly compared to PI cross sections unless the branching ratios for the various radiative decay channels are known. In this respect, the present situation is favorable, especially for the $3p^5 3d^2$ intermediate configuration, since it can safely be assumed that the radiative transition to the $3p^6 3d\ ^2D$ ground state (left

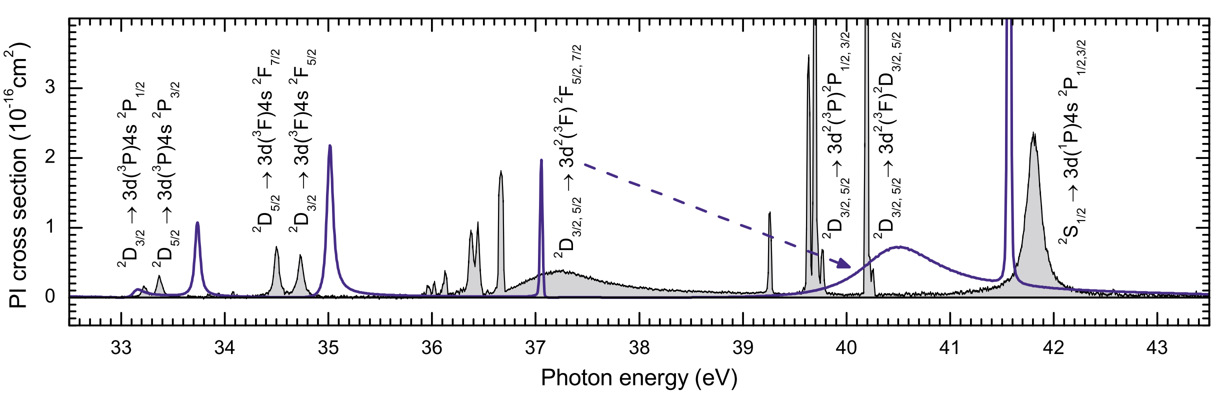

FIG. 1 (color online). Experimental (shaded curve) and theoretical (full line) [13] Sc^{2+} PI cross section in the energy range 32.5–43.5 eV. Resonances have been identified with the aid of atomic structure calculations [14]. In the designation of the resonances [Ar]$3d$ or [Ar]$4s$ have been omitted in the case of the $2D_{3/2}$, $2D_{5/2}$, and $2S_{1/2}$ initial states and [Mg]$3p^5$ in the case of the doubly excited intermediate states. The experimental energy spread is ~25 meV.

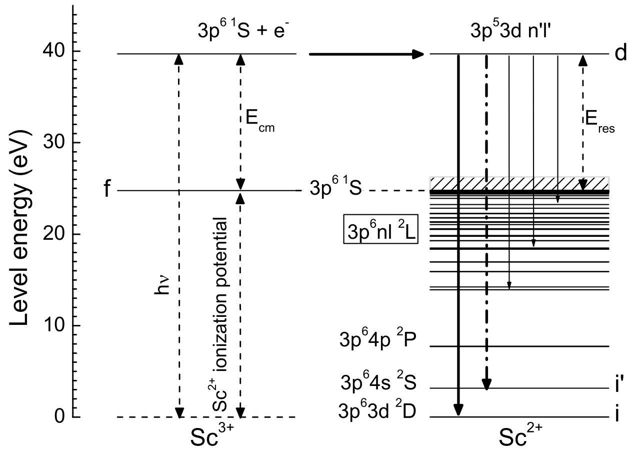

FIG. 2. Energy level diagram for the dielectronic (resonant) recombination of Sc^{3+} ions. Initially the ion in the $3p^6\,{}^1S$ ground state (f) collides with a free electron with energy $E_{\rm cm}$ above the first Sc^{2+} ionization threshold. If $E_{\rm cm} \approx E_{\rm res}$ a $Sc^{2+}(3p^5 3d\,n'l')$ doubly excited state (d) may be formed by dielectronic capture (inverse autoionization) with nonzero probability (horizontal full arrow). The recombination event is completed by a subsequent radiative transition to a bound state below the Sc^{2+} ionization threshold (vertical arrows). For $3p^5 3d^2$ and $3p^5 3d 4s$ doubly excited intermediate states the radiative decay paths to the PI initial states $3p^6 3d$ (i, thick full vertical arrow) and $3p^6 4s$ (i', thick dash-dotted vertical arrow) respectively ($3d \rightarrow 3p$ transitions) are unique; i.e., for the decay of $3p^5 3d^2$ and $3p^5 3d 4s$ states the multitude of other energetically allowed transitions (vertical thin full arrows) can be neglected (see text). On the scale of the figure fine-structure level splittings are not resolved.

vertical thick full arrow in Fig. 2) by far dominates all other transitions to excited $3p^6\,nl$ states (other left vertical arrows in Fig. 2). This assumption is supported by our atomic structure calculations and can qualitatively be understood by noting that for a transition to a $3p^6 3d$ state only one of the two $3d$ electrons in a $3p^5 3d^2$ state has to be moved, whereas for a transition to an excited $3p^6\,nl$ state additionally the second $3d$ electron has to be excited. From our atomic structure calculations we furthermore find that also the $3p^5 3d 4s$ states have a unique radiative decay path to the $3p^6 4s\ {}^2S$ excited state (again a $3d \rightarrow 3p$ transition, vertical thick dash-dotted arrow in Fig. 2). It should be emphasized that Sc^{2+} with a true one-to-one correspondence between PI and PR via low lying doubly excited states is quite unique. A more normal case, i.e., PI of C^{2+} and PR of C^{3+} ions, was investigated recently by Müller *et al.* [8].

TABLE I. Statistical weights g_i, ionization potentials I_i (from Ref. [16]) and lifetimes τ_i (from Ref. [17]) of the Sc^{2+} ground state and of the first two excited, metastable states. The fraction η_i of each state in the Sc^{2+} ion beam have been determined by comparing measured PI and PR cross sections.

State		g_i	I_i (eV)	τ_i (s)	η_i (%)
$3p^6 3d$	$2D_{3/2}$	4	24.756 84	∞	20.7 ± 3.0
$3p^6 3d$	$2D_{5/2}$	6	24.732 34	1.20×10^4	54.6 ± 4.3
$3p^6 4s$	$2S_{1/2}$	2	21.590 37	0.0514	24.7 ± 1.3

Having established that the radiative decay paths for the decay of the resonances shown in Fig. 1 are unique, we can construct partial recombination cross sections $\sigma^{\rm (PR)}_{f\rightarrow i}$ for the three separate recombination channels that end in each of the three initial PI states i. Partial PR cross sections are obtained by inserting the experimental PI cross section data (with the PI resonance energies shifted by the appropriate ionization energy I_i as given in Table I) into Eq. (1) and by carrying out summations over all doubly excited states d connected by a dipole transition to each given state i, yielding

$$\sigma^{\rm (PR)}_{f\rightarrow i}(E_{\rm cm}) = \frac{1}{\eta_i}\frac{g_i}{g_f}\frac{(E_{\rm cm}+I_i)^2}{2m_{\rm e}c^2 E_{\rm cm}}\sum_d L_{i\rightarrow d}(E_{\rm cm},\ldots), \quad (2)$$

with η_i denoting the fractional abundance of state i in the Sc^{2+} ion beam of the PI experiment. The resonance parameters to be inserted into the line profiles $L_{i\rightarrow d}(E_{\rm cm}, A_d, \Gamma_d, E_d, q_d)$, i.e., peak area A_d, width Γ_d, position E_d, and in the case of asymmetric line profiles also the Fano asymmetry parameter q_d [18], were determined by fitting line profiles to the measured PI resonances displayed in Fig. 1 [14]. Thereby, for the broad

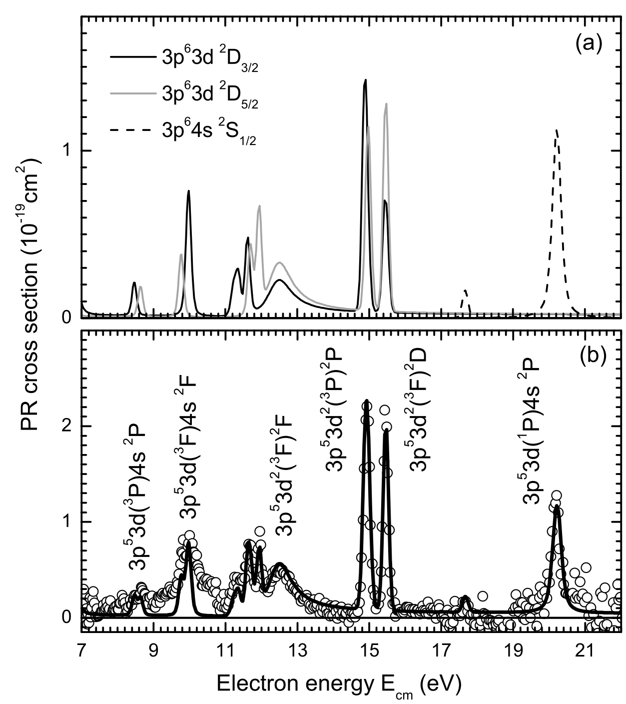

FIG. 3. Fit of the weighted sum of partial PR cross sections derived from the present PI measurements to the experimental PR cross section (open symbols) measured at the Heidelberg heavy-ion storage-ring TSR [11]. The resonance line shapes were convoluted with a normalized Gaussian representing the resolution of the Sc^{3+} PR experiment. The partial cross sections [cf. Eq. (2)] adding up to the total fit result [full line in (b)] are shown separately in (a).

$3p^5 3d^2\ ^2F$ resonance it has been assumed that the PI cross section is independent of the fine-structure splitting of the $3p^6 3d\ ^2D$ ground state, i.e., the same PI cross section parameters have been used for both the $^2D_{3/2}$ and the $^2D_{5/2}$ state.

The fractional abundances of the $3p^6 3d\ ^2D_{3/2}$ ground state and the $3p^6 3d\ ^2D_{5/2}$, and $3p^6 4s\ ^2S_{1/2}$ metastable states, in the following denoted by $\eta_{3/2}$, $\eta_{5/2}$, and $\eta_{1/2}$, respectively, are obtained from fitting the sum of the three partial PR cross sections (constructed from the present measurement) to the measured PR cross section of Schippers *et al.* [11]. From the fit, where the condition $\eta_{3/2} + \eta_{5/2} + \eta_{1/2} = 1$ was imposed, we obtain $\eta_{3/2} = 0.207$, $\eta_{5/2} = 0.546$, and $\eta_{1/2} = 0.247$. We note that the ratio 2.63 of $^2D_{5/2}$ to $^2D_{3/2}$ ions greatly exceeds the value 1.5 that is expected for a statistical level population. In the fit the unidentified resonances were included in the various partial cross sections such that the χ^2 of the fit was minimized. The uncertainties of the η_i values given in Table I partly reflect the change of η_i when the unidentified resonances are distributed in different ways among the three partial PR cross sections. It should be noted that, apart from the fractional abundances, the absolute PI cross section scale was also obtained from the same fit as another fit parameter.

The agreement between the measured and the fitted PR spectrum (Fig. 3) is excellent except for some PR resonance strength around 10 eV. It may be speculated that this PR resonance strength stems from transitions between higher excited states that were not included in the partial spectra. A further parameter varied during the fit was an energy offset allowing for matching the PR and the PI energy scales. Matching of the scales can be achieved by shifting the PR energy scale by 0.13 eV (within its experimental uncertainty [11]) towards higher energies. The uncertainty of the PI energy scale is of the order of a few meV.

The state-selective PI cross sections shown in Fig. 4 were readily obtained by converting the partial PR cross sections [Eq. (2)] via Eq. (1). The strongest resonance at $\sim$41.8 eV is due to $3p \rightarrow 3d$ excitation of the $3p^6 4s\ ^2S_{1/2}$ metastable state. Its oscillator strength amounts to 2.1 ± 0.4. Within the experimental error this value agrees with the one for the same transition in isoelectronic Ca^+ ions [3]. Comprehensive information will be given in a forthcoming publication [14].

In conclusion, by combining the high resolving power of a photoionization experiment at a synchrotron light source with the state selectivity available in a heavy-ion storage-ring experiment, we have derived photoionization cross sections of Sc^{2+} ions in the ground state and in two metastable states. An almost perfect one-to-one correspondence of PR and PI exists for the $3p^5 3d^2$ and $3p^5 3d 4s$ resonances. Consequently, the principle of detailed balance could be applied for the determination of the fractional composition of the Sc^{2+} ion beam. Absolute state-selective (on the fine-structure level) photoionization cross sections are thereby obtained on a purely experimental basis. With the present results we obtain, in addition, partial cross sections for photorecombination of Sc^{3+} ions proceeding to different final states. These data will permit a more sensitive comparison of state-of-the-art theory with experiment and thus challenge our present understanding of photorecombination and photoionization processes.

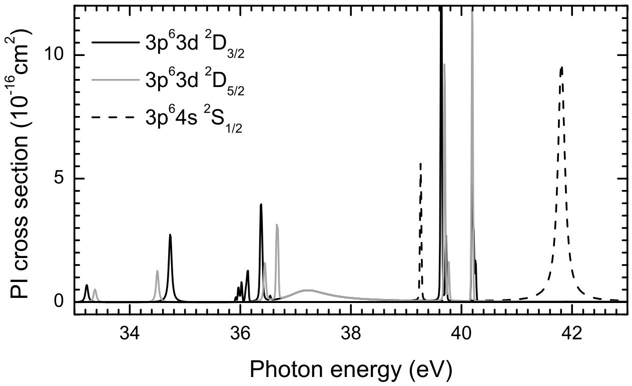

FIG. 4. State selective Sc^{2+} PI cross section. The systematic uncertainty of the cross section scale is $\pm 20\%$. The energy spread is 25 meV, i.e., approximately the same as in Fig. 1.

We gratefully acknowledge financial support through the NATO Collaborative Research Grants CRG-950911 (A. M., S. S.), CLG-976362 (S. R.), and from the Division of Chemical Sciences, Biosciences and Geosciences of the U.S. Department of Energy under Contract No. DE-FG03-97ER14787 (A. A., A. M. C., M. F. G., R. A. P.). G. H. D. was supported in part by U.S. DOE Contract No. DE-A102-95ER54293.

[1] E. Blanke *et al.*, Phys. Rev. Lett. **51**, 355 (1983).
[2] M. J. Seaton *et al.*, Mon. Not. R. Astron. Soc. **266**, 805 (1994).
[3] J. B. West, J. Phys. B **34**, R45 (2001).
[4] H. Kjeldsen *et al.*, Phys. Rev. A **62**, 020702(R) (2000).
[5] J.-M. Bizau *et al.*, Phys. Rev. Lett. **87**, 273002 (2001).
[6] A. M. Covington *et al.*, Phys. Rev. Lett. **87**, 243002 (2001).
[7] B. Kristensen *et al.*, Phys. Rev. A **65**, 022707 (2002).
[8] A. Müller *et al.*, J. Phys. B **35**, L137 (2002).
[9] Y. Itoh *et al.*, J. Phys. B **34**, 3493 (2001).
[10] D. Voulot *et al.*, J. Phys. B **33**, L187 (2000).
[11] S. Schippers *et al.*, Phys. Rev. A **65**, 042723 (2002).
[12] I. I. Sobelman, *Atomic Spectra and Radiative Transitions* (Springer-Verlag, Berlin, 1992).
[13] Z. Altun and S. T. Manson, J. Phys. B **32**, L255 (1999).
[14] S. Schippers *et al.* (to be published).
[15] R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981).
[16] NIST Atomic Spectra Data Base, http://physics.nist.gov/cgi-bin/AtData/main_asd
[17] C. J. Zeippen, Astron. Astrophys. **229**, 248 (1990).
[18] U. Fano, Phys. Rev. **124**, 1866 (1961).