Electron-capture cross section at near-thermal collision energies for $Si^{4+}+D$

Marc Pieksma,[1] M. Gargaud,[2] R. McCarroll,[3] and C. C. Havener[1]
[1]*Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6372*
[2]*Observatoire de l'Université de Bordeaux I, UA 352 du CNRS, Boîte Postal 89, 33720 Floirac, France*
[3]*Laboratoire de Dynamique Moléculaire et Atomique, UA 774 du CNRS, Université Pierre et Marie Curie, Tour 12 ES, 75252 Paris Cedex, France*
(Received 6 October 1995)

Using a merged-beams technique, absolute total electron-capture cross sections have been measured in the thermal energy regime for collisions of Si^{4+} ions with neutral D atoms. State-of-the-art molecular-orbital coupled-channel calculations for the $Si^{4+}+H(D)$ systems are compared to the measurements on an absolute scale. Both the existence of a surprisingly large kinematic isotope effect and an observed sharp low-energy increase of the cross section are attributed to trajectory effects due to an attractive ion-induced dipole. [S1050-2947(96)50507-X]

PACS number(s): 34.70.+e, 82.30.Fi

Current studies of electron-capture processes are motivated by the fact that they constitute reaction channels of fundamental importance in plasma environments, such as in fusion devices and stellar plasmas. Until recently, most experimental investigations of electron-capture processes by ions have been made at collision energies above 0.1 eV/amu (see, for example, [1–3]). At very low (thermal or near-thermal) energies there have been measurements of charge-transfer rate constants on a variety of systems (e.g., [4]), but, to our knowledge, there have been no direct measurements of electron-capture cross sections involving H or D, and hence, no direct tests of our understanding. Physical intuition for these processes tends to come from relatively simple models [5–7], which include predictions of a kinematic isotope effect where the cross section depends on the mass of the isotope used and a sharp increase of the cross section as the collision energy is decreased. However, the predicted scaling of these effects on the cross section is inconsistent between models. More involved fully quantal calculations predict that at thermal energies shape resonances may contribute to an enhancement of the cross section [8].

All of the phenomena just mentioned are related to the fact that, during the collision, the ion induces an attractive dipole in the neutral atom. The ion-induced dipole potential is given by

$$V(R) = -\frac{\alpha q^2}{2R^4}(\text{a.u.}), \tag{1}$$

where R is the internuclear distance, α is the polarizability of the neutral atom ($\alpha = 4.5$ a.u. for both H and D), and q is the charge of the ion. At low collision energies, the force due to potential (1), and the resulting acceleration of the particles towards each other, will significantly modify their trajectories. This results in the incident trajectories accessing smaller internuclear distances than the initial impact parameter.

When the collision energy is low enough, trajectory effects dominate the electron-capture process. This is the basis of the Langevin model [5]. According to this simple model, there exists a critical impact parameter b_c, such that for $b < b_c$ the trajectories follow collapsing orbits during which electron capture can occur. The Langevin model predicts that the cross section scales as $\sigma \propto q/v\sqrt{\alpha/\mu}$ [5], where v is the collision velocity and μ is the reduced mass. At low energies, then, the cross section is predicted to depend inversely on the collision velocity. In addition, the model shows that trajectory effects are stronger for collision systems with smaller reduced masses. This kinematic isotope effect leads to a larger electron-capture cross section when a lighter isotope is involved. The ratio of the cross sections for collision systems with different isotopes is predicted by the Langevin model to be inversely proportional to the square root of the ratio of the reduced masses.

This simple Langevin model is not expected to be appropriate since it does not fully address the collision physics at low energies [9]. Indeed, for symmetric collision systems where there are no crossings between initial and final states [like $H^+ + H(D)$], the Langevin model predicts a strong isotope effect, although no such effect exists [7,10,11]. While the Langevin model does treat trajectory effects (which leads to the $1/v$ dependence in the cross section), it assumes that capture will occur with a probability of unity sometime during the collapsing orbit. However, consider for example a two-state asymmetric system with one entrance and exit channel, where the capture process takes place at a specific crossing radius, R_x. The quantum-mechanical probability for capture then depends on, among other parameters, the radial velocity. At low enough energies and for $R_x < b_c/\sqrt{2}$ (collapsing orbit condition [5]), this radial velocity is determined by the ion-induced dipole attraction. For that reason the mass dependence of the isotope effect is more complicated than that given by the Langevin model.

A model that takes into account the couplings at potential-energy curve crossings that can result in transitions is the Landau-Zener-Stueckelberg model. While not providing accurate absolute cross sections, it can account for the classical trajectories of the heavy particles as modified by the ion-induced dipole potential [12,13]. Recently, this model was used to estimate the magnitude of the kinematic isotope effect in low-energy electron capture with a variety of multicharged ions [7]. These results indicate that at 0.1 eV/amu

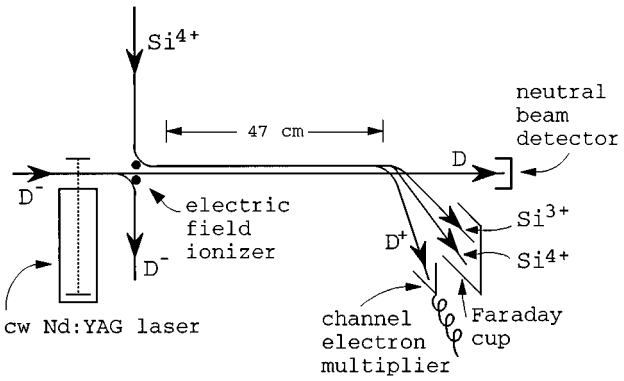

FIG. 1. A simplified schematic drawing of the ion-atom merged-beams setup.

the estimated cross section enhancement for collisions performed with H instead of D varies widely. Although the validity of this formalism at lower energies is not discussed [7], the results suggest an isotope effect that scales as one over the ratio of reduced masses, differing from the Langevin prediction.

Fully quantal calculations are considered most accurate, and allow a detailed comparison with experiment on an absolute scale. Very recently, quantal calculations have been reported and compared to available experimental data for the $N^{4+}+H(D)$ [7,14] and the $C^{3+}+H(D)$ [2,15] systems, but, even at the lowest measured collision energies for these two systems, the isotope effect was still too small (compared to the error bars) to be conclusively identified. We give here experimental support for the actual existence of strong trajectory and kinematic isotope effects in electron-capture processes at near-thermal collision energies.

Measurements of the electron-capture cross section of the $Si^{4+}+D$ system were performed using the Oak Ridge National Laboratory (ORNL) ion-atom merged-beams apparatus, which has been comprehensively described previously [12]. This apparatus is depicted schematically in Fig. 1. By merging two fast beams of neutral atoms and multiply charged ions, a large dynamic range of collision energies becomes available, allowing access to low collision energies where methods using static targets cannot be used. In the present investigation a variable-energy Si^{4+} beam was merged with a 7-keV D beam, and total electron-capture cross sections were measured in the energy range of 0.02–500 eV/amu. The center-of-mass collision energy follows from

$$E_{\mathrm{c.m.}}=\left[\frac{E_1}{m_1}+\frac{E_2}{m_2}\right]-2\sqrt{\frac{E_1E_2}{m_1m_2}}\cos(\theta), \tag{2}$$

where E_1 and m_1 refer to the energy (eV) and the mass (a.u.) of the neutral beam, and E_2 and m_2 to those of the ion beam. Included in E_1 and E_2 are the estimated plasma potential shifts of the duoplasmatron source (10 V) and the electron cyclotron resonance source (20 V per charge). In practice, the merge angle θ is very small, but it is of importance at thermal collision energies, where it limits the lowest center-of-mass energy that can be achieved.

The Si^{4+} beam is produced by the ORNL $2\omega_c$ CAPRICE electron cyclotron resonance (ECR) ion source. It has an intensity of 1–3 μA, a diameter of 2–4 mm (full width at half maximum), and a divergence less than 0.25^{o}, which is a significant improvement compared to previous experiments [2,12,14]. A fast neutral D atom beam is obtained by photodetachment of a 7-keV D^- beam extracted from a duoplasmatron source using a 1.06-μm cw neodymium-doped yttrium aluminum garnet (Nd:YAG) laser. The D beam is nearly parallel (the divergence is less than 0.15^{o}), has a diameter of about 2 mm, and an intensity of 10–20 nA.

The Si^{4+} beam is merged electrostatically with the neutral D beam. Both beams interact along a field-free region of 47 cm (see Fig. 1), after which the primary beams and the product D^+ ions are separated magnetically. The neutral beam is monitored by measuring secondary emission from a stainless steel plate, and the intensity of the Si^{4+} beam is measured using a Faraday cup. The product signal D^+ ions are detected by a channel electron multiplier. The absolute electron capture cross section is obtained from directly measurable parameters [12]:

$$\sigma=\frac{Sqe^2\gamma v_{\mathrm{D}}v_{\mathrm{Si}^{4+}}}{I_{\mathrm{D}}I_{\mathrm{Si}^{4+}}\varepsilon\langle F\rangle Lv}, \tag{3}$$

where S is the signal count rate, e is the electronic charge, γ is the secondary electron emission coefficient of the neutral beam detector, v_{D} and $v_{\mathrm{Si}^{4+}}$ are the velocities of the beams, I_{D} and $I_{\mathrm{Si}^{4+}}$ are the electrical beam intensities, ε is the efficiency for detecting D^+, $\langle F\rangle$ is the average beam overlap integral, L is the length of the merge path, and v is the relative velocity. The numerical value for γ was determined *in situ* to be 1.064 ± 0.023. The horizontal and vertical measurements of the beam overlaps (see Ref. [12] for details) were used to obtain the merge angles. Merge angles as small as 0.1^{o} were achieved.

Both the neutral and the ion beam contain unwanted constituents that contribute to the above signal. Specifically, this concerns D atoms in Rydberg states, resulting from stripping of D^- ions with background gas, a N^{2+} contamination of the Si^{4+} beam, and Si^{4+} metastables. As shown in Fig. 1, an electric-field ionizer (30 kV/cm) was used to quench excited D atoms whose electrons are in high-n shells (typically $n>12$), thereby reducing the correction [14] to the cross section to less than 10%. The percentage of N^{2+} ions in the Si^{4+} beam was determined by measuring the intensities of the N^{2+} isotopes and was found to be 4–7 %. Using published electron-capture cross sections for the $N^{2+}+H$ system [16], the estimated correction to the experimental cross sections was only 2–4 %. No correction could be made for the Si^{4+} metastables. However, the metastable fraction was reported to be as low as 5% [17].

In Fig. 2 the measured electron-capture cross section of the $Si^{4+}+D$ system is shown as a function of collision energy. The error bars on the experimental data indicate the statistical error at a 90% confidence level. At 2.9 eV/amu the total uncertainty is shown, which is a quadrature sum of the statistical error and the systematic error (12%, see Ref. [2]). For several low-collision-energy data points the uncertainty in the collision energy is also indicated. This uncertainty is estimated using Eq. (2) and the finite divergence of the

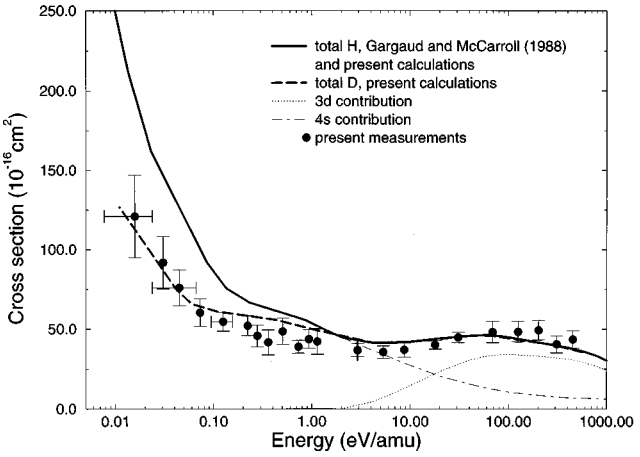

FIG. 2. A comparison of the dependence on the collision energy of the experimental and the theoretical total electron-capture cross sections of the $Si^{4+}+D$ system. Also included are theoretical calculations for $Si^{4+}+H$. See text for details.

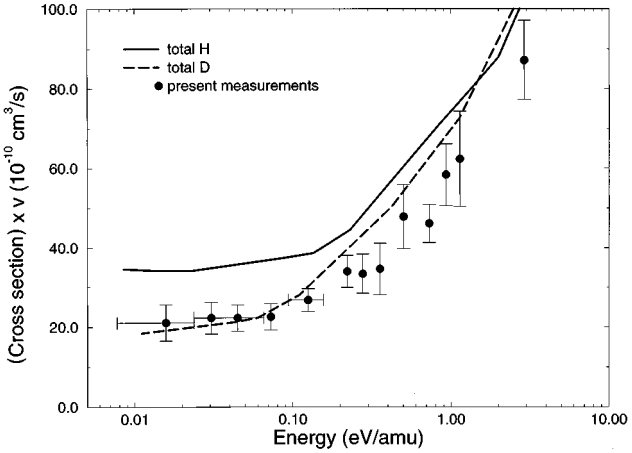

FIG. 3. The same data as in Fig. 2, but now showing the total electron-capture cross section times the collision velocity as a function of collision energy.

beams, the energy spread of the multicharged Si^{4+} beam due to the plasma of the ECR source (6.5 eV per charge as mentioned in Ref. [18]), the rms fluctuation of the ECR source high-voltage supply (6.5 V), and the energy spread of the neutral D beam due to the duoplasmatron (6 eV according to Ref. [19]).

Also shown in Fig. 2 are the results of theoretical calculations of the electron-capture cross sections of the $Si^{4+}+D$ and $Si^{4+}+H$ systems. Full details of the theoretical methods and the results for the $Si^{4+}+H$ system for collision energies above 1 eV/amu were previously published [20]. Only the essential features of the method will be recalled here. A model potential is used to represent the Si^{4+} core, and the effective one-electron two-center Hamiltonian of the SiH^{4+} molecular ion is diagonalized in a basis set of Slater-type orbitals to generate electronic adiabatic energies, wave functions, and non-adiabatic matrix elements of the system. The Si^{4+} ion core model potential is defined by a set of parameters optimized to reproduce the Si^{3+} energy levels with a precision better than 0.01%. Translation effects are taken account of by the introduction of appropriate reaction coordinates [21,22]. The coupled equations for the nuclear motion are then solved in a fully quantal formulation. Prior to integration, the adiabatic states are transformed to a diabatic representation [23].

When the experimental results for $Si^{4+}+D$ are compared with electron-capture cross-section calculations for the same system, excellent agreement is found, as Fig. 2 demonstrates. Up to now, measurements of electron-capture cross sections reported in the literature have not been able to observe isotope effects for collision systems involving H and D atoms at the lowest collision energies that were experimentally achievable (0.1 eV/amu) [2,12,13]. However, as can be seen from Fig. 2, after extending the calculations for $Si^{4+}+H$ to energies far below 1 eV/amu, a dramatic difference of almost a factor of 2 is found. It should be pointed out that measurements below 1 eV/amu with H rather than D atoms could not be performed because of the limited dynamic range of the ECR source. Still, we want to emphasize that the comparison between absolute experimental cross sections and absolute calculated cross sections, as shown in Fig. 2, provides good evidence for the existence of a kinematic isotope effect in the electron-capture process of slowly colliding multicharged ions and neutral atoms.

Note from Fig. 2 that at low collision energies capture into the $Si^{3+}(4s)$ state (via radial coupling, and with an exoergicity of $Q=7.3$ eV [20]) is the only open channel, while at the higher energies the main channel is capture into the $Si^{3+}(3d)$ state (via rotational coupling, and with $Q=11.9$ eV [20]). The isotope effect applies therefore to electron capture into one particular state [namely $Si^{3+}(4s)$].

Although the agreement between theory and experiment is very good, it might seem from Fig. 2 that between 0.1 and 1 eV/amu some data points are slightly lower compared to theory. In this energy region the angular acceptance of the apparatus for the product D^+ ions should be sufficient, even though significant angular scattering of the D^+ ions might occur in the center-of-mass frame [24]. For the estimated angular acceptance of 2.3^o in the laboratory frame, calculations for $O^{5+}+D$ indicate that all signals will be collected for collision energies below 1 eV/amu, even if maximum (90^o) scattering would occur in the center-of-mass frame [6]. Measurements at low energies with the current apparatus for this system, which does exhibit relatively large angular scattering [25], have shown good agreement with theory [6]. Most likely, any small differences between theory and experiment can be attributed to the Si^{4+} metastable fraction. Still, since theory and experiment are completely consistent with each other within their uncertainties, it is concluded that the effect of these metastables on the present results is acceptably small.

In order to analyze the behavior of the electron-capture cross section at low collision energies in more detail, in Fig. 3 the cross section times the collision velocity is plotted. A $1/v$ velocity dependence (the Langevin limit) is reached once this quantity becomes constant. Indeed, one observes that below a collision energy of 0.1 eV/amu the experimental results show a flat region, and that, within error bars, this

behavior is fully consistent with our theoretical calculations for $Si^{4+}+D$. Calculations for $Si^{4+}+H$ are also shown. The cross section for H compared to D is shown to be a factor of 1.9 larger, in contradiction to the Langevin model, which predicts a factor of only 1.4. This failure of the Langevin model to predict the magnitude of the isotope effect is due to the fact that it does not take into account the quantum-mechanical transition probability for capture, and that this probability is different for collisions involving H and D.

The Langevin model, though, does correctly predict the $1/v$ velocity dependence, even though it fails to include the transition probability. Physical intuition provided by the Langevin model tells us that a $1/v$ increase in the cross section occurs when the ion-induced dipole attraction dominates the incident trajectories. At these energies the transition probability is independent of the incident velocity, which means that the radial velocity at the time of transition is determined by the attractive force of the dipole. This radial velocity is dependent on the mass, which leads, as discussed above, to the failure of the Langevin model to predict the correct isotope effect.

In conclusion, electron-capture cross sections of a multiply charged ion interacting with a deuterium atom have been measured down to thermal collision energies, using a state-of-the-art merged-beams technique. These measured cross sections have been compared with the results of our theoretical calculations on an absolute scale. Below a collision energy of 1 eV/amu this comparison provides evidence for a strong kinematic isotope effect, and for a $1/v$ behavior of the electron-capture cross section at very low collision energies. Both of these effects are due to trajectory effects caused by the ion-induced dipole interaction. The calculated low-energy limit for the reaction rates for the different isotopes was not as predicted by the simple Langevin model. The isotope effect is more complicated due to the fact that quantum-mechanical couplings exist between initial and final states.

The authors would like to thank S.Y. Ovchinnikov and M. Minear for fruitful discussions, and A.C.H. Smith and F.W. Meyer for critically reading the manuscript. This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, Contract No. DE-AC05-84OR21400 with Lockheed Martin Energy Systems, Inc. M.P. acknowledges support from the Netherlands Organization for Scientific Research (NWO).

[1] R.A. Phaneuf, Phys. Rev. A **24**, 1138 (1981).
[2] C.C. Havener, A.M. Müller, P.A. Zeijlmans van Emmichoven, and R.A. Phaneuf, Phys. Rev. A **51**, 2982 (1995).
[3] H. Saitoh, K. Soejima, S. Kravis, K. Okuno, and N. Kobayashi (unpublished).
[4] D. Smith, N.G. Adams, E. Alge, H. Villinger, and W. Lindinger, J. Phys. B **13**, 2787 (1980).
[5] G. Giomousis and D.P. Stevenson, J. Chem. Phys. **29**, 294 (1958).
[6] C.C. Havener, F.W. Meyer, and R.A. Phaneuf, in *Invited Papers of the Seventeenth International Conference on the Physics of Electronic and Atomic Collisions, Brisbane, 1991*, edited by W.R. MacGillivray, I.E. McCarthy, and M.C. Standage (AIP, New York, 1992), p. 381.
[7] P.C. Stancil and B. Zygelman, Phys. Rev. Lett. **75**, 1495 (1995).
[8] N. Shimakura and M. Kimura, Phys. Rev. A **44**, 1659 (1991).
[9] M. Henchman, in *Ion-Molecule Reactions*, edited by J.L. Franklin (Wiley-Interscience, New York, 1972), Vol. I, p. 185.
[10] J.B. Delos, Rev. Mod. Phys. **53**, 287 (1981).
[11] V.A. Belyaev, B.G. Brezhnev, and E.M. Erastov, Zh. Éksp. Teor. Fiz. **52**, 1170 (1967) [Sov. Phys. JETP **25**, 777 (1967)].
[12] C.C. Havener, M.S. Huq, H.F. Krause, P.A. Schultz, and R.A. Phaneuf, Phys. Rev. A **39**, 1725 (1989).
[13] C.C. Havener, M.S. Huq, F.W. Meyer, and R.A. Phaneuf, J. Phys. (Paris) Colloq. **50**, C1-7 (1989).
[14] L. Folkerts, M.A. Haque, C.C. Havener, N. Shimakura, and M. Kimura, Phys. Rev. A **51**, 3685 (1995).
[15] B. Herrero, I.L. Cooper, A.S. Dickinson, and D.R. Flower, J. Phys. B **28**, 4607 (1995).
[16] F.G. Wilkie, F.B. Yousif, R.W. McCullough, J. Geddes, and H.B. Gilbody, J. Phys. B **18**, 479 (1985).
[17] J.S. Thompson and D.C. Gregory, Phys. Rev. A **50**, 1377 (1994).
[18] T.A. Antaya, J. Phys. (Paris) Colloq. **50**, C1-707 (1989).
[19] L.E. Collins and R.H. Gobbett, Nucl. Instrum. Methods **35**, 277 (1965).
[20] M. Gargaud and R. McCarroll, J. Phys. B **21**, 513 (1988).
[21] M. Gargaud, R. McCarroll, and P. Valiron, J. Phys. B **20**, 1555 (1987).
[22] R. McCarroll and D.S.F. Crothers, Adv. At. Mol. Opt. Phys. **32**, 253 (1994).
[23] M. Gargaud, J. Hanssen, R. McCarroll, and P. Valiron, J. Phys. B **14**, 2259 (1981).
[24] R.E. Olson and M. Kimura, J. Phys. B **15**, 4231 (1982).
[25] L. Andersson, M. Gargaud, and R. McCarroll, J. Phys. B **24**, 2073 (1991).