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Electron Capture Cross Sections For TiH^{4+}

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Electron capture cross sections for TiH^{4+}

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Abstract. Electron capture cross sections have been computed for $\text{Ti}^{4+} + \text{H} \rightarrow \text{Ti}^{3+} + \text{H}^+$ and $\text{Ti}^{3+} + \text{H}^+ \rightarrow \text{Ti}^{4+} + \text{H}$, where the reactants were in their ground states. The energy range investigated was 0.1 to 10 keV amu^{-1} . The impact parameter perturbed-stationary-state method incorporating electron translation factors was used to calculate the cross sections. The molecular wavefunctions were generated using the pseudo-potential method. At 1 keV amu^{-1} ($v_{\text{rel}} = 4.4 \times 10^7 \text{ cm s}^{-1}$), representative electron capture cross sections for the $\text{Ti}^{4+} + \text{H}$ and $\text{Ti}^{3+} + \text{H}^+$ reactions are $2 \times 10^{-15} \text{ cm}^2$ and $1 \times 10^{-17} \text{ cm}^2$, respectively. An appreciable energy dependence was observed for both cross sections.

1. Introduction

The investigation of multiply-charged ion-atom collisions is a very active area of research. Advances have been made in both experimental and theoretical methods, thus allowing comparisons to be made between theory and experiment. The importance of including electron translation factors in the molecular treatment of electron capture reactions has been recognised (for example, Riera and Salin 1976), especially if one expects to calculate the partial cross sections for the products of the reaction. For partially stripped ion systems, the use of model or pseudo-potential methods has been shown to be invaluable (Gargaud *et al* 1981) in the calculation of accurate energies and wavefunctions.

Little theoretical work has been directed to the heavy multiply-charged ion-atom systems except for early calculations by Salop and Olson (1979) on the $\text{Fe}^{26+} + \text{H}$ reaction. Most work has been directed to the $Z \leq 8$ ion systems. The cross sections for the heavier ions, however, are of considerable interest to magnetically confined fusion plasma research since the container wall is made from stainless steel which, besides Fe, has significant concentrations of Ti, Cr and Ni. Electron capture collisions of ground-state ions with protons

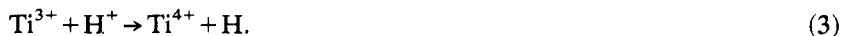


are important. These collisions are deleterious to confinement times if the cross sections exceed 10^{-18} cm^2 .

In this work we present calculated cross sections for the electron capture reactions



and



For reaction (2), the Ti^{4+} has an Ar closed-shell structure, while in (3) the Ti^{3+} ground state is $(\text{Ar})3d^2D$. Thus, these reactions are pseudo-one-electron systems which are amenable to the use of pseudo-potential techniques. The use of electron-translation factors removes spurious long-range couplings and permits the prediction of the cross sections for the product states of (2) and (3).

2. Theoretical method

2.1. Molecular wavefunction

The wavefunctions and potential energies for the TiH^{4+} system were computed using the pseudo-potential molecular structure method. Since Ti^{4+} is an argon-like ion, it is possible to replace the potential produced by its core electrons and nucleus by a pseudo-potential and reduce the molecular calculations to a one-electron problem. Such techniques are well established and have been described fully (Bardsley 1974).

The Schrödinger equation for the valence electron of the TiH^{4+} molecular ion is given by

$$\left(\frac{1}{2}\nabla_r^2 + V_A(\mathbf{r}_A) - \frac{1}{r_B} + \frac{4}{R} - E_j(R)\right)\Phi_j(\mathbf{r}, R) = 0 \quad (4)$$

where \mathbf{r}_A and \mathbf{r}_B are the position vectors of the electron with respect to the Ti^{4+} and H^+ nuclei, respectively. Atomic units are used unless otherwise stated. The eigenvalues $E_j(R)$ and eigenfunctions $\Phi_j(\mathbf{r}, R)$ depend on the internuclear separation R and $V_A(\mathbf{r}_A)$ represents the interaction between the valence electron and the Ti^{4+} electron core. This latter term is replaced by a pseudo-potential. We have chosen to use an l -dependent Gaussian-type pseudo-potential of the form

$$V(\mathbf{r}) = \sum_{l,m} V_l(r) |Y_{lm}\rangle \langle Y_{lm}| \quad (5)$$

with

$$V_l(r) = A_l \exp(-\xi_l r^2) - \frac{\alpha_d}{2(r^2 + d^2)^2} - \frac{4}{r} \quad (6)$$

where $|Y_{lm}\rangle$ are the spherical harmonics. The parameters A_l and ξ_l have been determined from the recent spectroscopic data of Corliss and Sugar (1979). Hartree-Fock calculations were used to estimate the cut-off radius d . The dipole polarisability α_d was taken from the review by Dalgarno (1962). Numerical values for the pseudo-potential parameters are given in table 1.

Table 1. Ti^{4+} pseudo-potential parameters (in atomic units).

A_0	21.378 489
A_1	12.122 318
A_2	-8.310 281 8
ξ_0	1.260 747 3
ξ_1	0.938 907 75
ξ_2	1.975 230 1
d	0.5
α_d	1.62

The electronic wavefunction $\Phi_j(\mathbf{r}, \mathbf{R})$ is constructed using a two-centre expansion in terms of a linear combination of atomic orbitals. Fixed orbital exponents in a Slater-type orbital (STO) basis were employed. The form of $\Phi_j(\mathbf{r}, \mathbf{R})$ is given by

$$\Phi_j(\mathbf{r}, \mathbf{R}) = \sum_i c_{ij} X_i^{\text{STO}}(\mathbf{r}_A) + \sum_i d_{ij} X_i^{\text{STO}}(\mathbf{r}_B). \quad (7)$$

A complete one-electron configuration-interaction calculation was performed.

The orbital exponents of the STO are given in table 2. The $Ti^{3+}(3d)$ orbital exponents were taken from the work of Clementi and Roetti (1974). The 4s and 4p triple-zeta and the 4d single-zeta exponents were determined by optimising to the lowest energy of the respective ionic levels. Using the above basis set, the differences between the calculated and spectroscopic energy levels of Ti^{3+} are 0.015, 0.036, 0.009 and 0.002 eV for the 3d, 4s, 4p and 4d levels, respectively. The hydrogen atomic orbitals are exact for the 1s and $n = 2$ levels, with an additional tight 2p orbital added to improve the accuracy of the dipole polarisability of the ground state of hydrogen.

Table 2. Orbital exponents of Slater-type orbital basis functions.

Ti^{3+}	3d	9.199	H	1s	2.000	
		4.452			1.000	
		3.457			0.500	
		2.227			0.500	
					2s	0.500
					2p	1.000
	4s	4.958		0.500		
		3.489				
		1.887				
	4p	5.184				
		2.827				
		1.655				
	4d	1.258				

The calculated potential energy curves are given in figure 1. The ${}^2\Sigma$, ${}^2\Pi$ and ${}^2\Delta$ states have been included in this calculation. There is an outer avoided crossing between the $Ti^{4+} + H$ and the $Ti^{3+}(4d) + H^+$ levels at $R \approx 15.5a_0$. The major interaction for the scattering calculation arises from an avoided crossing between the state diabatically connected to the $Ti^{4+} + H$ level and the states asymptotically connected to $Ti^{3+}(4p) + H$.

2.2. Scattering calculation

The scattering calculations were performed using the perturbed-stationary-state (PSS) method (Bates *et al* 1953), modified to include electron translation factors (ETF). In such a method, the heavy particles are assumed to move classically, while the electronic motion is treated quantum mechanically. The total wavefunction is expanded as

$$\psi(\mathbf{r}, t) = \sum_i a_i(t) \Phi_i(\mathbf{r}, \mathbf{R}) F_i(\mathbf{r}, \mathbf{R}) \quad (8)$$

where $\Phi_i(\mathbf{r}, \mathbf{R})$ is the Born–Oppenheimer wavefunction from the pseudo-potential

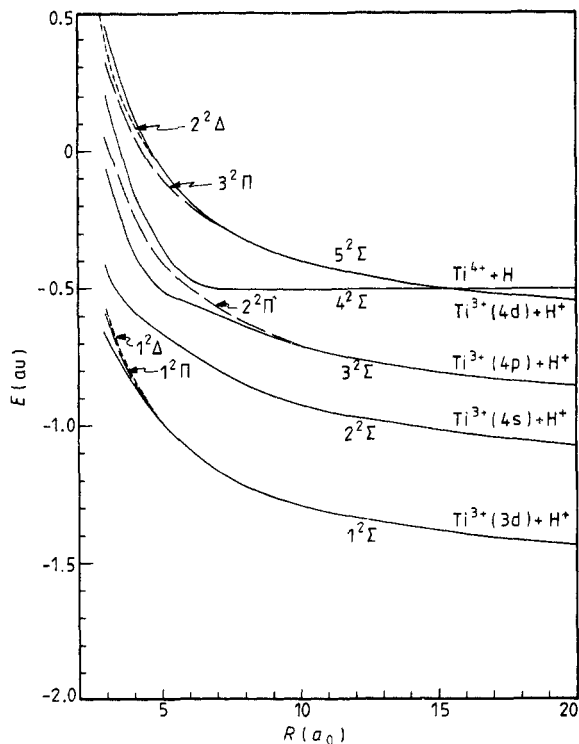


Figure 1. Potential energy curves for the TiH^{4+} system.

calculations with eigenvalue $E_i(R)$. The electron translation factors have the form

$$F_i(\mathbf{r}, \mathbf{R}) = \exp\left(\frac{1}{2}i f_i(\mathbf{r}, \mathbf{R}) \mathbf{r} \cdot \mathbf{v}\right) \quad (9)$$

where \mathbf{v} is the relative velocity of the heavy particles and $f_i(\mathbf{r}, \mathbf{R})$ represents a switching function that incorporates the two-centre molecular character into the ETF (Delos and Thorson 1979, Kimura and Thorson 1981).

Substituting equation (8) into the time-dependent Schrödinger equation leads to the set of coupled equations

$$\dot{a}_j(t) = \sum_{i \neq j} \mathbf{v} \cdot (\mathbf{P} + \mathbf{A})_{ji} a_i \exp\left(-i \int^t (E_i(t') - E_j(t')) dt'\right) \quad (10)$$

where we have expanded the ETF, equation (9), in powers of v and have retained the first-order ETF correction terms. Here, \mathbf{P} and \mathbf{A} are the non-adiabatic coupling and ETF correction terms, respectively. The dot product in a rotating-frame coordinate system is

$$\mathbf{v} \cdot (\mathbf{P} + \mathbf{A}) = \dot{\mathbf{R}}(\mathbf{P}^R + \mathbf{A}^R) + \dot{\theta}(\mathbf{P}^\theta + \mathbf{A}^\theta) \quad (11)$$

with

$$P_{ji}^R = \left\langle j \left| i \frac{\partial}{\partial \mathbf{R}} \right| i \right\rangle \quad (12a)$$

$$A_{ji}^R = \frac{1}{2}i \left\langle j \left| f_i \frac{\partial}{\partial z} \right| i \right\rangle \quad (12b)$$

$$P_{ji}^0 = \langle j | \hat{L}_y | i \rangle \quad (12c)$$

and

$$A_{ji}^0 = \frac{1}{2} R i \left\langle j \left| f_i \frac{\partial}{\partial x} \right| i \right\rangle. \quad (12d)$$

The first term of the right-hand side of equation (11) represents the radial coupling, while the second term is the rotational (angular) coupling. The radial and angular velocities can be written as

$$\dot{R} = \frac{v_0 Z}{R} \quad (13a)$$

and

$$\dot{\theta} = \frac{b v_0}{R^2} \quad (13b)$$

if one assumes the straight-line approximation. In equation (13), b is the impact parameter and v_0 is the relative velocity of the collision.

Representative radial and rotational coupling matrix elements are shown in figure 2. All the coupling matrix elements were evaluated numerically using 12-point Gauss-Laguerre and Legendre quadratures.

The $(\mathbf{P} + \mathbf{A})$ matrix elements used in the coupled equation are invariant to the choice of the electron coordinate. The coupling matrix elements do not have spurious behaviour at large internuclear separations, making it possible to provide the partial cross sections to the individual electron capture product states. The cross sections were evaluated using standard techniques after the amplitudes a_j were determined.

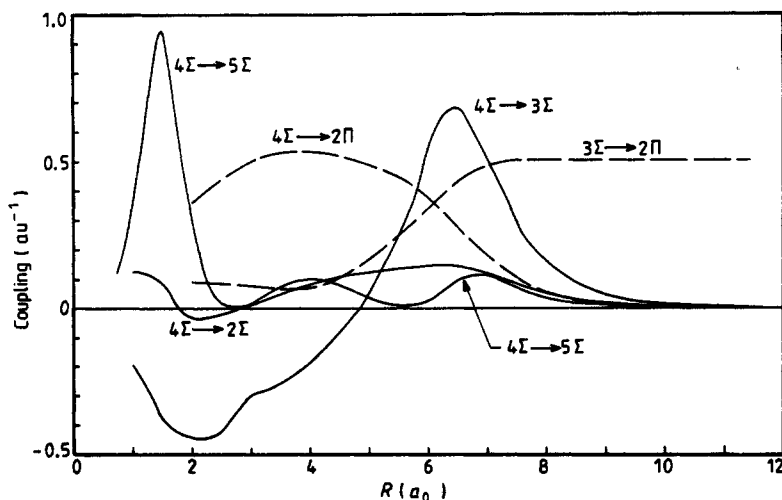


Figure 2. Abbreviated set of the ETF corrected coupling matrix elements. The full and broken curves denote radial and rotational coupling terms, respectively.

3. Cross sections

The cross sections were evaluated using the PSS method with the ten lowest molecular states of the TiH^{4+} ion (shown in figure 1). All possible combinations of the radial

and rotational coupling terms were included in the coupled-channel calculations. The integrations were carried out between $R = \pm 12a_0$. It was verified, using a Landau-Zener calculation, that the particles passed diabatically through the outer avoided crossing at $R \approx 15.5a_0$ between the $\text{Ti}^{4+} + \text{H}$ and $\text{Ti}^{3+}(4d) + \text{H}^+$ states. At $R = 15.5a_0$, the potential difference between the $^2\Sigma$ states was 0.0002 au. Even at the lowest velocity studied, the calculations indicated that the contribution from the outer avoided crossing to the electron capture cross section for reaction (2) will not exceed $1 \times 10^{-16} \text{ cm}^2$. This does not imply that the $\text{Ti}^{3+}(4d)$ level is not populated during the collision since interactions on the repulsive wall of the potential are important. With a large uncertainty, our calculations indicate the $\text{Ti}^{3+}(4d)$ partial cross section is about $1 \times 10^{-16} \text{ cm}^2$ at 1 keV amu^{-1} . At higher collision energies, this cross section increases due to stronger coupling at small R values.

The electron capture cross sections for the $\text{Ti}^{4+} + \text{H}$ reaction are shown on figure 3. The dominant collision mechanism is strong radial and rotational coupling from the $4^2\Sigma$ state to the $3^2\Sigma$ and $2^2\Pi$ states at $R \approx 6a_0$. The strength of this coupling is highly energy dependent, leading to a threefold increase in the cross section from 0.1 to 1.0 keV amu^{-1} . The major final state is $\text{Ti}^{3+}(4p)$; the partial cross section for the production of this excited level is given on figure 3. The large energy dependence of the total cross sections indicates that, in many cases, cross section predictions based

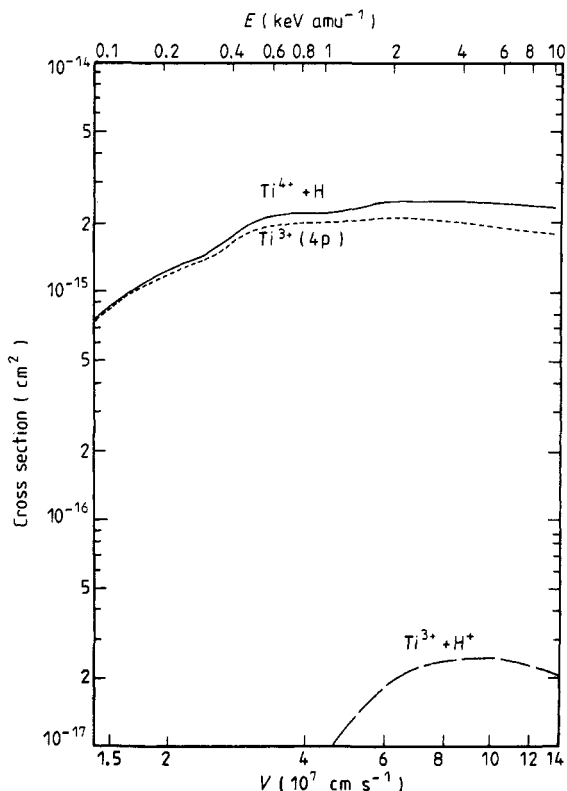


Figure 3. Electron capture cross sections for $\text{Ti}^{4+} + \text{H}$ and $\text{Ti}^{3+} + \text{H}^+$, reactions (2) and (3). The broken curve is the partial cross section for producing $\text{Ti}^{3+}(4p) + \text{H}^+$ in $\text{Ti}^{4+} + \text{H}$ collisions.

on simple scaling procedures will be inapplicable to the low charge states of the heavy ions. Such behaviour is also the case for the light ions ($Z \leq 8$).

One of the more interesting aspects of our study was the investigation of the electron capture cross section for the ground-state ion-proton reaction, $Ti^{3+} + H^+$. Very little is known about these processes at energies of interest to the fusion community ($E \approx 1$ to 10 keV amu^{-1}). Fusion experts hope that the ion-proton electron capture cross section will not exceed 10^{-18} cm^2 , since larger values lead to the prediction of unacceptably low confinement times. Impurity ions in the plasma will lead to H^+ (or D^+) being converted to H (or D) and then lost to the container walls.

We have begun our studies with the $Ti^{3+}(3d) + H^+$ reaction. The calculated cross sections are shown on figure 3 and are found to be about $2 \times 10^{-17} \text{ cm}^2$ in the 2 to 10 keV amu^{-1} region. The mechanism is stepwise loss of flux to the multitude of higher-lying levels by the collisions that probe the repulsive wall of the potentials. Rotational coupling, accompanied to a lesser extent by radial coupling, eventually leads to loss to the electron capture state, $Ti^{4+} + H$.

Trajectory effects were investigated for the $Ti^{3+} + H^+$ reaction. Cross sections calculated using curvi-linear trajectories determined by a repulsive $+3/R$ potential were compared with those obtained from straight-line trajectories. At 1 keV amu^{-1} , the use of curvilinear trajectories decreased the cross section by 15%. At 5 keV amu^{-1} , the decrease in the cross section was less than 6%.

The $Ti^{3+} + H^+$ calculations indicate there may be a serious loss of H^+ (or D^+) from a fusion plasma by electron capture collisions with partially stripped impurity ions. The ion-proton cross sections are determined by stepwise excitation in small impact parameter collisions. Hence, it is reasonable to assume the largest cross sections will arise in collisions of H^+ with low charge-state ions since there are fewer excitation transfer states between the entrance and the electron capture channels. Likewise, the heavy impurity ions will have larger cross sections than the low- Z ions because the repulsive wall of the potential extends to a greater internuclear distance, which allows mixing at larger impact parameters.

4. Conclusions

The pseudo-potential molecular structure method was used to calculate the approximate eigenvalues and eigenfunctions for the low-lying states of TiH^{4+} . Radial and rotational coupling matrix elements, corrected by electron translation factors, were computed from the eigenfunctions. The perturbed-stationary-state method with ten coupled channels was used to determine the electron capture cross sections for the $Ti^{4+} + H$ and $Ti^{3+} + H^+$ reactants. Both cross sections were highly dependent on the collision energy, indicating that simple cross section scaling models are inappropriate for this system. The electron capture cross section for ground-state $Ti^{3+} + H^+$ was calculated to be $2 \times 10^{-17} \text{ cm}^2$ at 2 to 10 keV amu^{-1} , implying partially-stripped impurity ion-, proton-electron capture collisions may have an adverse effect on magnetically confined fusion plasmas.

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