Electron capture in low-energy collisions of Si³⁺ with He

D Rabli[1], M Gargaud[2] and R McCarroll[1]

[1] Laboratoire de Dynamique des Ions Atomes et Molécules (ESA 7066 CNRS), Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris 5, France
[2] Observatoire de l'Université de Bordeaux I BP 89 (UMR 5804 CNRS), 33270 Floirac, France

Abstract
Cross sections and rate coefficients for selective electron capture in Si³⁺/He collisions in the thermal-eV energy range have been calculated using a model potential representation of the ionic cores and a quantum mechanical description of the collision dynamics. The new calculated rate constants for Si³⁺/He are in excellent agreement with recent calculations of Stancil *et al* (Stancil P C, Clarke N J, Zygelman B and Cooper D 1999 *J. Phys. B: At. Mol. Opt. Phys.* **32** 1523) and are consistent with the ion-trap measurements of Fang and Kwong (Fang Z and Kwong V H S 1997 *Astrophys. J.* **483** 527).

(Some figures in this article are in colour only in the electronic version; see www.iop.org)

1. Introduction

Electron capture by Si^{q+} ions in thermal collisions with He is most simply described using the notion of non-adiabatic transitions at avoided curve crossings of the electronic states of the SiHe^{q+} molecular ion. Stancil *et al* [1] and Opradolce *et al* [2] have used a theoretical model of this kind for the Si⁴⁺/He system. Butler and Dalgarno [3], Honvault *et al* [4] and Stancil *et al* [5] have studied the Si³⁺/He system using a similar technique. By and large, the different theoretical calculations for the rate constants of both Si⁴⁺/He and the Si³⁺/He systems are fairly consistent with each other.

On the other hand, it is difficult to reconcile the theoretical results with certain of the ion-trap experiments. The most serious disagreement concerns the Si⁴⁺/He system, for which the measured rate constant of Fang and Kwong [6] is negligibly small ($\leqslant 10^{-12}$ cm³ s⁻¹) compared with the calculated value of around 10^{-9} cm³ s⁻¹. It is unlikely that there is anything fundamentally wrong with the theoretical calculations, especially since the same theoretical models have been used with success in interpreting ion-beam experiments for other ion–atom systems of a similar kind, such as Ar⁶⁺/He [7] and Ar⁸⁺/He [8]. Fang and Kwong [6] discount the possible presence of metastable Si⁴⁺ ions (or of N²⁺ ions with the same charge-to-mass ratio) present in the trap. So, there still remains a puzzling dilemma.

It may be observed that a similar problem in reconciling theory with the ion-trap measurements is encountered in the O²⁺/He system [9]. In that case a negligible charge transfer rate constant was also measured. However, there is both theoretical and experimental

evidence showing that ground state O^{2+} ions react rapidly with He (even though O^{2+} ions in the metastable ^1D state do not). Imperfections of the theory might explain a small discrepancy with experiment, but the measured rate constants in the ion-trap experiments are smaller than the theoretical values by a factor of the order of 1000 for the Si^{4+}/He and O^{2+}/He systems.

The situation is very different for Si^{3+}/He. In that case, the measured rate constant of 6×10^{-10} cm^3 s^{-1} is consistent with theory (experiment being some 30% above the theoretical calculations of Stancil *et al* [5] and Butler and Dalgarno [3] and a factor of three larger than the calculated values of Honvault *et al* [4]). Of course, a detailed comparison is still a little delicate, since the theoretical rate constant exhibits a fairly rapid variation with temperature in the 10^3–10^5 K range and there are problems in defining an effective temperature in the ion-trap experiments.

The objective of this paper is to analyse the difference between the various theoretical calculations. From the network of reaction channels in the Si^{3+}/He system [4, 5], it is clearly established that at low energies, electron capture takes place primarily to the ground $(3s^2)^1S$ state of Si^{2+} via the $^2\Sigma$ avoided crossing with the entry channel at 6 a_0. From the earlier calculations, it is seen that there is a maximum in the cross section for a centre-of-mass energy of around 17 eV (an ion energy in the laboratory system of 120 eV). For higher energies, the calculated cross sections are not very dependent on the height of the radial coupling peak value $A(R_x)$. However, with decreasing energy (smaller than the Landau–Zener maximum), the cross section depends quite critically on $A(R_x)$. It may be remarked that as a general rule, $A(R_x)$ is related to the minimum energy separation Δ_x in the case of an isolated avoided crossing according to the formula

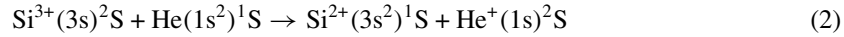$$A(R_x) = \frac{q-1}{2} \frac{1}{R_x^2 \Delta_x}. \tag{1}$$

The calculations of Honvault *et al* [4] do not seem to have been completely optimized for the energy separation at the curve crossing and their minimum energy separation is not compatible with (1). So while their results are reliable for energies above a centre-of-mass energy of 10 eV, they are susceptible to error for lower energies. On the other hand, in the more recent calculations of Stancil *et al* [5] the radial coupling peak and minimum energy separations are compatible with (1).

Rather than attempt to refine the *ab initio* calculations, we have opted in this work for a model potential method for the calculation of the molecular parameters. Our experience with this type of method, initially developed for systems with one active electron, has shown that it is also very satisfactory in dealing with isolated long-distance crossings in systems involving multiply charged ions and neutral He, provided proper account is taken account of the symmetry of equivalent electrons in the initial (and final) state. For example, when corrected in this way, the calculations of Opradolce *et al* [2] yield minimum energy separations for the Si^{4+}/He system in excellent agreement with Stancil *et al* [1], implying that, at the level of the Landau–Zener approximation, the model potential and *ab initio* methods should yield almost identical electron capture cross sections. We have therefore every reason to believe that such a model potential method should also be reliable for Si^{3+}/He. Besides, in a model potential method, the minimum energy separations and the radial coupling matrix elements can be calculated exactly within the limitations of the method. If necessary, translation effects can be simply accounted for [10, 11].

On the other hand, it is obvious from our above remarks, that our theoretical model, like all others [1, 2], cannot offer any satisfactory explanation of the large discrepancy between theory and experiment for electron capture in the Si^{4+}/He system. For that reason, we have not deemed it worthwhile to reinvestigate this system at the present time.

2. Method

The method is similar to that used for the treatment of the Ar^{6+}/He system of Gargaud *et al* [7], which is an extension of the method introduced by Grice and Herschbach [12] for treating long-range configuration interaction in collisions between neutral atoms to deal with avoided crossings in multiply charged ions and atoms. In the case of the reaction

$$\text{Si}^{3+}(3\text{s})^2\text{S} + \text{He}(1\text{s}^2)^1\text{S} \rightarrow \text{Si}^{2+}(3\text{s}^2)^1\text{S} + \text{He}^+(1\text{s})^2\text{S} \tag{2}$$

it is easily shown that to a good approximation the energy levels and radial coupling matrix elements of the two Σ states correlated to the initial and final channels can be obtained as eigenvalues of the one-electron model Hamiltonian

$$H_m = T + V_{\text{Si}^{3+}} + V_{\text{He}^+} + U_c \tag{3}$$

where $T + V_{\text{Si}^{3+}}$ is the model Hamiltonian describing the 3s orbital in the final $(3\text{s}^2)^1\text{S}$ state of Si^{2+} and $T + V_{\text{He}^+}$ the model Hamiltonian of the 1s orbital in the initial $(1\text{s}^2)^1\text{S}$ state of He. It is also implicitly assumed that the overlaps of the 3s orbital of Si^{3+} with the 3s orbital of Si^{2+} and of the 1s orbital of He$^+$ with the 1s orbital of He are practically unity. This has been verified to within a few per cent. The core–core interaction is designated by U_c in (3). Since the core polarization is relatively unimportant for the charge transfer process, U_c may be taken as

$$U_c = \frac{3}{R}. \tag{4}$$

In practice, for the two cores we have used model potentials expressed in the form

$$V(r) = -\frac{q}{r} - \frac{1}{r}\sum_i Z_i(c_i, r)\exp(-d_i r) \tag{5}$$

where q is the ionic core charge and Z_i is defined by the expressions

$$Z_1 = 1 + c_1 r \tag{6}$$

$$Z_2 = 2 + c_2 r \tag{7}$$

$$Z_3 = 2 + 3c_3 r + 2(c_3 r)^2 + 2(c_3 r)^3 \tag{8}$$

$$Z_4 = 6 + 9c_4 r + 6(c_4 r)^2 + 2(c_4 r)^3. \tag{9}$$

The parameters c_i and d_i are obtained by optimizing [13] the eigenvalues of the model atomic Hamiltonian to the experimental energies of the ground and the few excited states of the Si^{2+} ion. These parameters take account of screening of the nucleus by the inner 1s, 2s and 2p shells. However, little physical significance can be attached to any one specific parameter since several independent sets of parameters can usually be found to reproduce the experimental data adequately. Previous calculations [14] show that any set of parameters which satisfy the optimization criterion can be used for the molecular calculations.

The c_i and d_i parameters are listed in table 1 and the corresponding eigenvalues of the atomic model Hamiltonian are compared in tables 2 and 3 with the experimental values [15].

Table 1. Model potential parameters.

	q	c_1	d_1	c_2	d_2	c_3	d_3	c_4	d_4
He$^+$	1	1.666	3.636	—	—	—	—	—	—
Si^{+2}	3	7.909	11.128	49.550	12.167	0.94	2.017	0.25	8.47

Table 2. Comparison of experimental $Si^{2+}(3snl)^1S$ energies with calculated values (au).

nl	Moore	Model potential
1s	—	−59.340
2s	—	−4.609
2p	—	−2.770
3s	−1.229	−1.228
3p	−0.852	−0.851
3d	−0.673	−0.672
4s	−0.505	−0.505
4p	−0.426	−0.396
4d	−0.299	−0.333

Table 3. Comparison of experimental $He(1snl)^1S$ energies with calculated values (au).

nl	Moore	Model potential
1s	−0.903	−0.904
2s	−0.146	−0.158
2p	−0.124	−0.127
3s	−0.061	−0.066
3p	−0.055	−0.056
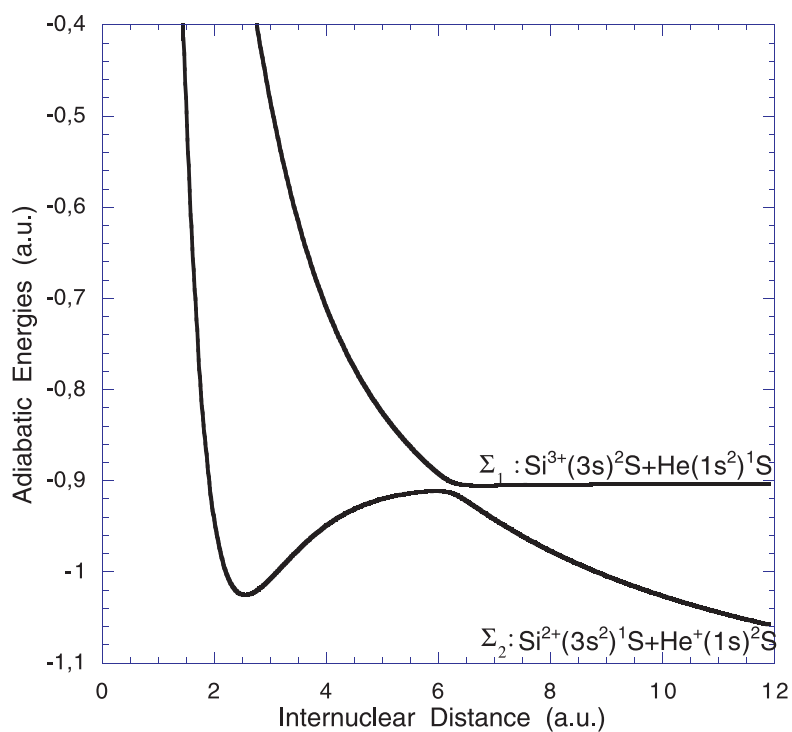
Figure 1. Adiabatic energies as a function of internuclear distance.

The spectrum of the Hamiltonian (3) is determined by a standard variational method using a set of Slater orbitals. We present in figure 1 the corresponding potential energy curves.
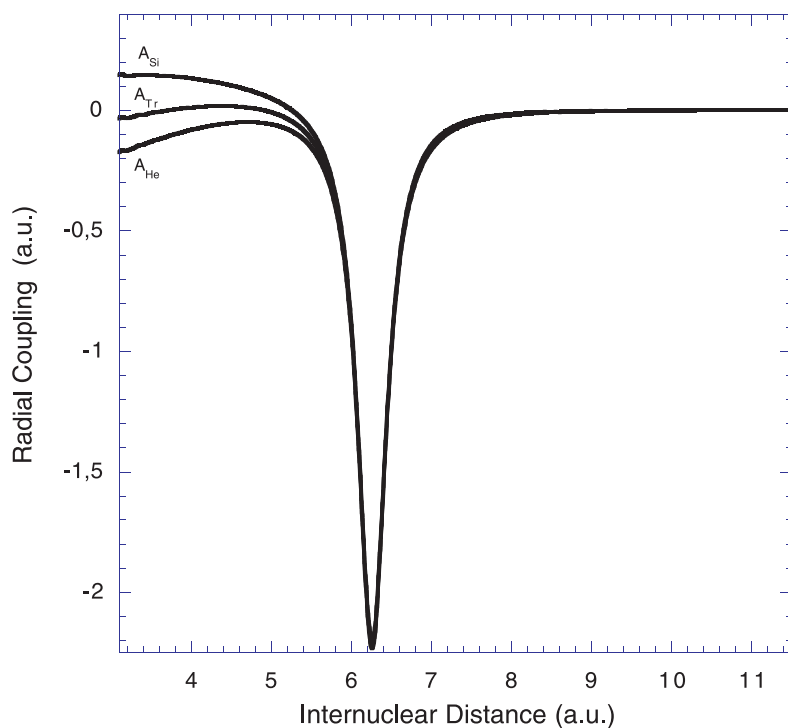
Figure 2. Three variants of the radial coupling matrix element A_{Si}, A_{He} and A_{Tr}.

Our adiabatic energies exhibit an avoided crossing between the entrance channel Σ_1 and the exit channel Σ_2: Si^{2+}(3s^2) + He$^+$(1s) which confirms that the electronic capture occurs via the 3s^2 ground state of Si^{2+} in conformity with the *ab initio* calculations of Honvault *et al* [4] and those of Stancil *et al* [5]. Our potential model calculations localize this Σ_1–Σ_2 avoided crossing at an internuclear distance $R_x = 6.28$ au with a corresponding energy separation $\Delta_x = 0.33$ eV.

At short distances ($R \sim 3$ au), the *ab initio* calculations exhibit a second avoided crossing which can lead to a possible electronic excitation in the 3p state of Si^{2+}. Our calculations using the potential model technique which considers the core to play a passive role cannot describe such an avoided crossing.

From an analysis of the *ab initio* results of Stancil *et al* [5] and those of Honvault *et al* [4], it is easily seen that the contribution to the total electronic capture cross section due to this avoided crossing remains unimportant over the entire range energy considered in this paper. Even for a collision energy value about 290 eV amu^{-1} it does not exceed 0.6%.

The radial coupling element was determined using the finite difference technique. We present in figure 2 three variants of the radial coupling matrix element A_{Si}, A_{He} and A_{Tr}. The first two, A_{Si} and A_{He}, refer, respectively, to calculations with the electronic origin taken to be on the Si and the He nucleus. The third, A_{Tr}, independent of the electronic origin is calculated using appropriate reaction coordinates [11]. These curves give some idea of the localization of the avoided crossing. On the other hand, it is easily seen that the translation effect is negligible for this system.

In table 4 we compare our curve-crossing parameters and the intensity of the radial coupling element with the results of Honvault *et al* [4] and Stancil *et al* [5]. On the basis

Table 4. Comparison of model potential curve crossing and the intensity radial coupling.

	R_x (au)	Δ_x (eV)	$A(R_x)$ (au)
Present work	6.28	0.33	2.25
Honvault *et al*	6.00	0.25	1.80
Stancil *et al*	6.3	0.27	2.5

of this comparison, we may expect the model potential method to yield reliable results for the collision dynamics.

3. Results

A quantum mechanical description of the collision dynamics has been adopted, following the procedure of Gargaud *et al* [16]. Prior to integration of the coupled state differential equations, the adiabatic states are transformed to the diabatic representation. Galilean invariance is ensured by the use of appropriate reaction coordinates [17] (equivalent to the use of the common translation factors of Errea *et al* [18]). The electron capture cross sections are listed in table 5. A comparison of the results with those of Honvault *et al* [4] and of Stancil *et al* [5] is presented in graphical form in figure 3.

Table 5. Si^{3+}/He capture cross section in units of 10^{-16} cm^2.

E (eV amu^{-1})	Total cross section
7.85×10^{-4}	18.65
2.32×10^{-3}	7.90
3.89×10^{-3}	5.50
5.82×10^{-3}	4.40
7.85×10^{-3}	3.93
0.0389	4.28
0.058	4.98
0.0778	5.73
0.155	7.92
0.233	9.96
0.388	11.88
0.582	13.54
1.25	16.03
2.50	16.85
4.357	16.77
10.00	15.30
22.503	12.91
40.00	11.13
62.52	9.70
124.96	7.83
187.94	6.98
250.00	6.49

The rate constant k_{ct} for charge transfer has been calculated from the cross sections by averaging over a Maxwellian distribution of the collision partners. The results are presented in tabular form in table 6 and in graphical form in figure 4, together with experimental and other theoretical values. In making a comparison between the different theoretical models, it should be borne in mind that our present calculations take no account of the influence of non-adiabatic
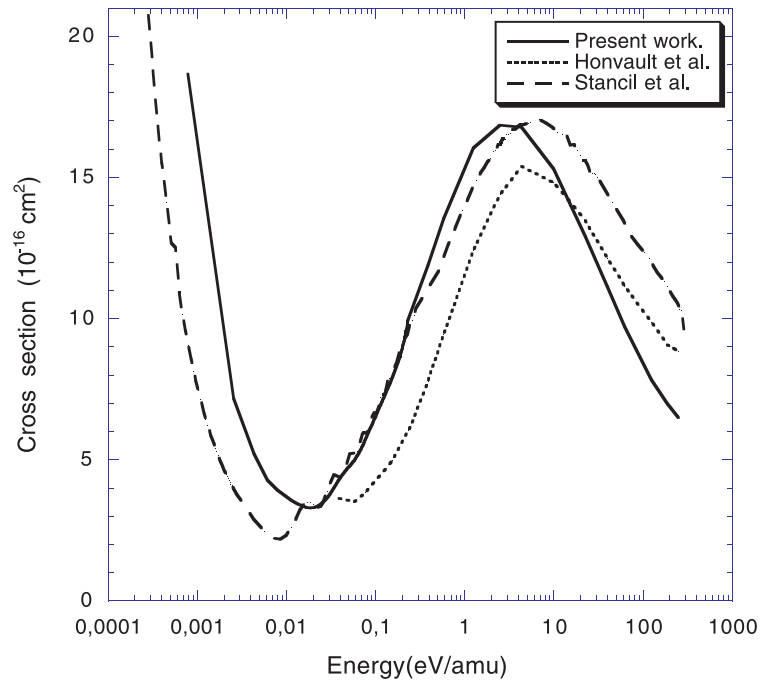
Figure 3. Si^{3+}/He total electron capture cross section (10^{-16} cm^2) as a function of laboratory energy.

Table 6. Si^{3+}/He electron capture rate coefficient (10^{-9} cm^3 s^{-1}).

T (K)	Present work	Stancil *et al* [5]	Honvault *et al* [4]	Butler *et al* [3]	Fang *et al* [20]
3	1.21×10^{-1}	—	—	—	—
5	1.09×10^{-1}	—	—	—	—
10	9.38×10^{-2}	—	—	—	—
20	8.02×10^{-2}	—	—	—	—
50	6.44×10^{-2}	—	—	—	—
100	5.63×10^{-2}	2.92×10^{-2}	—	—	—
200	5.51×10^{-2}	—	—	—	—
500	7.34×10^{-1}	6.34×10^{-1}	—	—	—
1 000	1.17×10^{-1}	1.15×10^{-1}	0.2×10^{-1}	1.7×10^{-1}	—
2 000	2.14×10^{-1}	2.17×10^{-1}	0.6×10^{-1}	—	—
4 000	4.09×10^{-1}	4.07×10^{-1}	—	—	6.3×10^{-1}
5 000	5.01×10^{-1}	—	2.1×10^{-1}	—	—
10 000	9.10×10^{-1}	8.81×10^{-1}	4.8×10^{-1}	9.6×10^{-1}	—
20 000	1.54	1.48	1.0	—	—
30 000	2.03	1.96	1.46	2.00	—
40 000	2.42	2.36	—	—	—
50 000	2.76	2.71	2.19	—	—
100 000	3.95	4.06	3.59	—	—

coupling with the excited $^2\Sigma^+$ state, whose asymptotic separated atoms correspond to the Si^{3+}(3p)^{2}P + He(1s^2) channel. This channel is closed for centre-of-mass energies below 8 eV and in the thermal energy range of astrophysical interest (10^2–10^5 K), its influence is negligibly
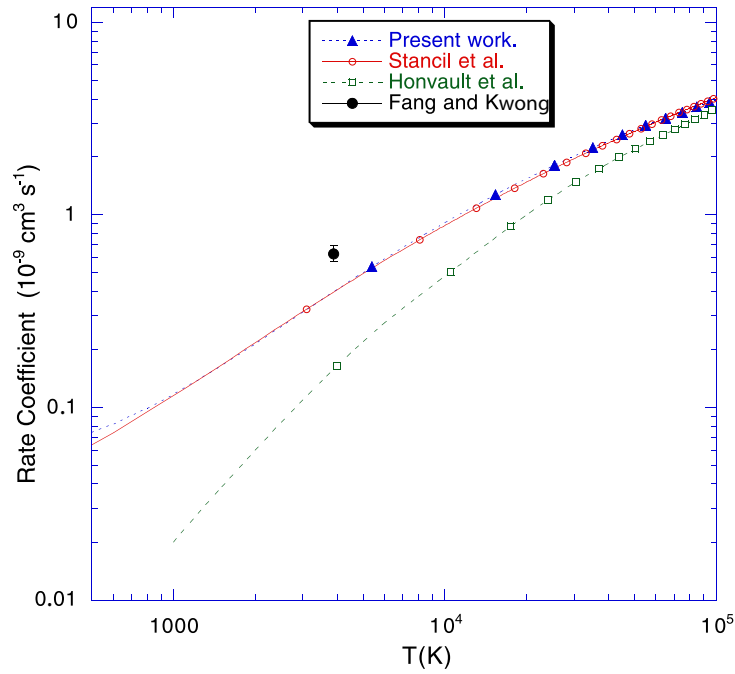
Figure 4. Si^{3+}/He reaction rate as a function of temperature (10^{-9} cm^3 s^{-1}).

small. Indeed, the calculations of Honvault *et al* [4] indicate that the two-state model should be valid up to energies of the order of 120 eV amu^{-1} (well beyond the excitation threshold). For energies less than the excitation threshold of the $Si^{3+}(3p)^2P + He(1s^2)$ channel Stancil *et al* [5] used a two-state model. In this energy range, where the cross section undergoes a strong variation with energy, their results are in excellent agreement with ours. The discrepancy at very low energies (less than 0.01 eV) is of little physical significance. The upturn of the cross section at 0.02 eV amu^{-1} is an indication of a Langevin-type trajectory effect [19], which depends sensitively on very long-range interactions. It would seem that the results of Honvault *et al* [4] are about 30% too low in the physically interesting region (0.1–10 eV amu^{-1}).

For energies above the excitation threshold Stancil *et al* [5] used a five state model and their calculated cross sections tend to be larger than ours for energies greater than about 10 eV amu^{-1}. Since these energies lie outside the astrophysically interesting temperature range of 10^2–10^5 K, we have not deemed it worthwhile to go beyond the two-state model in this work. However, it is surprising that the difference with Stancil *et al* [5] should be so large, given that the two-state model is expected to be valid up to the highest energies presented in table 5.

Our calculated charge transfer rate constants (for the whole range of temperatures studied) are in excellent agreement with Stancil *et al* [5] and they are also consistent with the experimental result of Fang and Kwong [20] (bearing in mind the difficulty of defining the effective temperature in the ion-trap experiment). It may be asked why the theory agrees well with experiment for this system and not for Si^{4+}/He. We have no explanation to offer, except to note that the Si^{3+} ion is perhaps a better choice for ion-trap experiments. Its charge-to-mass ratio is unlikely to be confused with any other ion (unlike Si^{4+} which has the same charge ratio as N^{2+}) and having an open shell structure, there is less risk of contamination with metastable

states. There is also good agreement with the earlier results of Butler *et al* [3], based on the Landau–Zener formula with semi-empirical molecular parameters.

4. Conclusion

There is an excellent agreement between the calculations of Stancil *et al* [5] based on *ab initio* methods for the determination of the molecular parameters (adiabatic energies and non-adiabatic coupling matrix elements) and our calculation based on model potential methods. This confirms the accuracy of model potential techniques (when properly employed) to treat charge transfer processes at thermal-eV energies.

Although there are still a few unexplained features of the calculated cross sections in the 10–100 eV amu^{-1} range, all evidence suggests that calculated thermal rate constants for charge exchange in the Si^{3+}/He system are now established to adequate precision in the temperature range from 10^2–10^5 K.

References

[1] Stancil P C, Zygelman B, Clarke N J and Cooper D L 1997 *Phys. Rev.* A **55** 1064
[2] Opradolce L, McCarroll R and Valiron P 1985 *Astron. Astrophys.* **148** 229
[3] Butler S E and Dalgarno A 1980 *Astrophys. J.* **241** 838
[4] Honvault P, Bacchus-Montabonel M C, Gargaud M and McCarroll R 1998 *Chem. Phys.* **238** 401
[5] Stancil P C, Clarke N J, Zygelman B and Cooper D 1999 *J. Phys. B: At. Mol. Opt. Phys.* **32** 1523
[6] Fang Z and Kwong V H S 1995 *Phys. Rev.* A **51** 1321
[7] Gargaud M, McCarroll R and Benmeuraiem L 1995 *Phys. Scr.* **51** 752
[8] Benmeuraieum L 1987 *Thèse de Doctorat*, Université de Bordeaux 1 No d'ordre 154
[9] Gargaud M, Bacchus-Montabonel M C and McCarroll R 1993 *J. Chem. Phys.* **99** 4495
[10] McCarroll R and Crothers S F 1994 *Adv. At. Mol. Opt. Phys.* **32** 253
[11] Delos J B 1981 *Rev. Mod. Phys.* **53** 287
[12] Grice R and Herschbach D R 1974 *Mol. Phys.* **27** 159
[13] Valiron P 1976 *Thèse de 3eme cycle*, Université de Bordeaux 1 No d'ordre 1279
[14] Gargaud M, McCarroll R and Opradolce L 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21** 521
[15] Moore C E 1949 *Atomic Energy Levels (NBS Circular no 467)* (Washington, DC: US Govt Printing Office)
[16] Gargaud M, Hanssen J, McCarroll R and Valiron P 1981 *J. Phys. B: At. Mol. Phys.* **14** 2259
[17] Gargaud M, McCarroll R and Valiron P 1987 *J. Phys. B: At. Mol. Phys.* **20** 1555
[18] Errea L F, Mendez L and Riera A 1982 *J. Phys. B: At. Mol. Phys.* **15** 101
[19] Pieksma M, Gargaud M, McCarroll R and Havener C C 1995 *Phys. Rev.* A **54** R13
[20] Fang Z and Kwong V H S 1997 *Astrophys. J.* **483** 527