Comparison of Charge Transfer in Proton Collisions with Methane and Silane for Simulations of Cold Plasma Impurities

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(Received 19 November 2007 / Accepted 9 January 2008)

Theoretical cross sections values for electron capture by proton impacting on methane and silane molecules are presented, based on the multi-reference single- and double-excitation configuration interaction calculation of electronic structures of collision intermediates, and compared with the available semi-empirical formulas recommended for fusion plasma simulations. The current results may apply not only to the simulations of fusion edge plasmas, but also plasmas of technological interest.

Keywords: electron capture, hydrocarbons, molecular orbital close coupling, silanium, methanium

DOI: 10.1585/pfr.3.S1040

1. Introduction

Carbon and Silicon are representative nonmetallic tetravalent elements important in applied plasma research, the former prevalent as plasma impurity originating, for instance, from carbon fiber composites used for the wall material of fusion reactor [1], the latter for its role in coagulation and growth of thin silicon-based films in industrial plasmas. The fully hydrogenated molecules of methane, its positively charged ions and derived fragments including highly reactive radicals co-exist in fusion edge plasmas. In addition, hydrogen–methane–silane plasmas have been used for production of nanoparticles [2]. It is the purpose of this work to provide a comparison of cross sections for electron capture in collision of proton with silane and methane in the keV/u collision energy region, which are mediated predominantly through transitions among the electronic states of intermediate off-equilibrium methanium CH_5^+ and silanium SiH_5^+ inheriting momentarily geometry of the original methane and silane, respectively. Within such setting, the rovibrational motion has been slow with respect to the typical collision time scale; the corresponding energy spacing is also minor compared to the energy of the projectile, and consequently accurate estimates of total charge transfer cross sections can be obtained by solving the coupled equations for transition amplitudes and nuclear wave functions within the representation of electronic states for several representative collision trajectories. The calculated cross sections for charge transfer in proton collision with CH_4were published previously and compared with experimental data. These are accompanied here by a new calculation for SiH_4,and both compared to semi-empirical formulae by Janev and Reiter [3] derived from the measured cross sections available in the literature [4]. The close coupling analysis is known to apply well to the vibrational ground-state of the target ion, which is well represented by the equilibrium molecular geometry, while the transitions from vibrationally excited states would require more detailed potential energy surface; in both cases the resolution of final post-collision states or calculation of branching ratios requires the account of asymptotic energy levels for all relevant couplings along with inclusion of vibronic couplings. Therefore the cross section values obtained in this framework are resolved only with respect to the electron capture onto the impacting proton. Given the high density of electronic states on the heavy molecular core, the excited states of hydrogen are usually very high (out of reach for most ab initio methods) based on the variational principle. The above approximations have been found quite plausible for a variety of collision systems within the keV/u collision energy region.

2. Methanium and Silanium

The cross sections for elastic and inelastic processes in H^++CH_4 collision were calculated before by Kimura *et al*. [5] and compared to new experimental values in a series of measurements on proton collisions with hydrocarbons by Kusakabe *et al*. [6], therefore only a brief summary is provided here. The specific process dealt with has been the exothermic collision

$$H^+ + CH_4(v = 0) \rightarrow H(1\,s,^2\,S) + CH_4^+(v = 0) + 0.618\,eV, \quad (1)$$

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Table 1 Cross section values for electron capture by proton in collision of H^++CH4 [6].

E (eV)	200	300	450	1000	2000	4000
$\sigma(10^{-16}\text{cm}^2)$	30.3	25.0	23.4	21.9	20.0	15.8

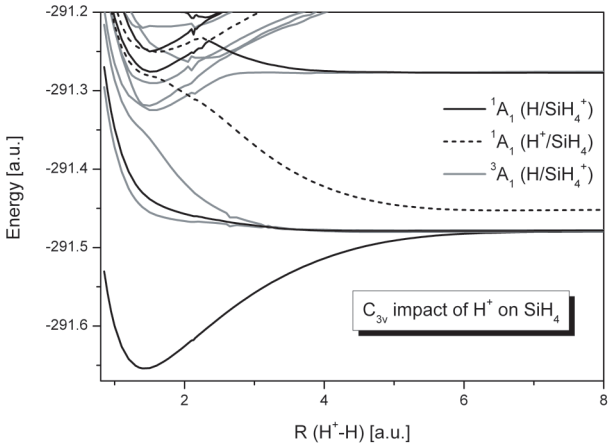

Fig. 1 Potential energy curves of A_1 symmetry for singlet and triplet states of silanium (atomic units of energy in Hartree and length in Bohr radius, a.u., are used).

for which the contribution of mixed vibrationally excited states of the target molecule at room temperature was estimated at about 20% level for typical experiment. The total of statistical and systematic uncertainties in the most recent measurement of absolute cross sections was also confined within the 20% margin [6]. Table 1 summarizes the experimental cross section values reproduced by the full quantum calculation [5, 6].

The cross section for electron capture on silane calculated in this work are based on a process corresponding to Eq. (1),

$$H^+ + SiH_4(\text{eq}) \rightarrow H(1\,\text{s},^2\,\text{S}) + SiH_4^+(\text{eq}) + 0.788\,\text{eV}. \quad (2)$$

Here the equilibrium geometry of silane has been used for the ab initio description of the collision system, namely Hydrogen nuclei coordinates are [0,0,*t*] [0,0,0] [0,*a*,-*b*] [-*c*,-*d*,-*b*], [*c*,-*d*,-*b*] with *t* being the impact trajectory distance, $a = 2.609$, $b = 3.690$, $c = 2.260$, $d = 1.305$ (all in atomic units, a.u.). The Silicon atom is placed at [0,0,-2.768]. The collision intermediate is subject to C_{3v} group symmetry, namely the incoming proton impacts onto one Si-H bond. The ab initio calculation of singlet and triplet electronic states of A_1 symmetry has been performed by Multi-reference single- and double-excitation configuration interaction method (MRD-CI) [7–10] following the standard procedures for collision physics applications [11]. Table 2 lists the asymptotic charge assignment for the lowest roots sorted in ascending order with energy.

Table 2 Charge state asymptotics of the lowest states of silanium collision complex.

	Symmetry (C_{3v}point group)	
Root Number	$^1A_1$	$^3A_1$
1	H/SiH_4^+	H/SiH_4^+
2	H/SiH_4^+	H/SiH_4^+
3	H^+/SiH_4	H/SiH_4^+
4	H/SiH_4^+	H/SiH_4^+
5	H^+/SiH_4	H/SiH_4^+
6	H/SiH_4^+	H/SiH_4^+
7	H/SiH_4^+	

Table 3 Cross section values for electron capture by proton in collision of H^++SiH4.

E (eV)	50	69	90	131	201	325
$\sigma(10^{-16}\text{cm}^2)$	10.36	13.56	16.33	16.88	17.68	20.23
E (eV)	4999	1000	2008	3081	4987	8073
$\sigma(10^{-16}\text{cm}^2)$	23.98	22.64	19.09	17.21	15.97	15.26

Both fully quantum-mechanical and semiclassical approaches within a molecular representation have been employed for describing the scattering dynamics driven by nonadiabatic couplings [11]. The total wave function for scattering in a quantum mechanical approach is described as a product of the electronic and nuclear wave functions, while in the semiclassical framework it further reduces to a product of a time-dependent coefficient and the electronic wave function. From technical viewpoint, coupled differential equations of second order for nuclear wave functions are obtained in the former approach, and coupled differential equations of first order for wave function amplitudes are obtained in the latter one. The numerical solution of the coupled system directly provides scattering matrix and transition probabilities in the partial wave (or impact parameter) expansion, which are then aggregated into the final cross sections as described in more detail in the previous series of papers on hydrocarbons [12].

Table 3 provides sampling cross section values calculated within the above approximation in semiclassical adiabatic framework appropriate for the energy range (cf. also Fig. 2).

3. Comparison with Available Formulae

The data need for accurate charge transfer cross sections in proton collisions with both methane and silane molecules has been stated in the series of Juelich reports by Janev and Reiter [3], who provide semi-empirical formulas for charge transfer in collisions of proton with CH_4,

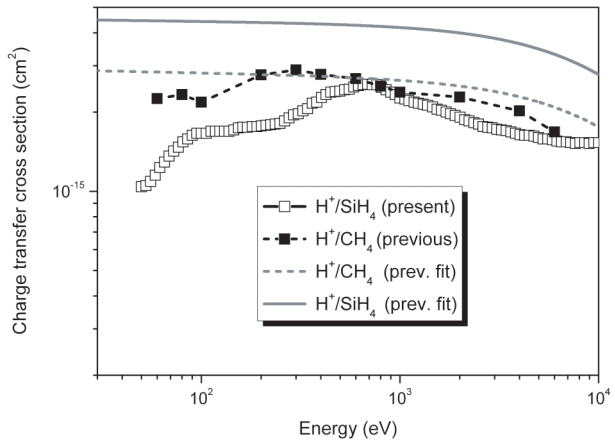

Fig. 2 Charge transfer cross sections: comparison of previous data for methane target (black dashed line, [5]), present results for silane target (full black line), and the semi-empirical formulae of Juelich report (gray lines, [3]).

$$\sigma_{CX} = \frac{9.96}{\sqrt{E} + 85E^{2.5}} + \frac{30.2}{E^{0.015} + 9.0\times10^{-6}E^{1.2} + 2.19\times10^{-18}E^{3.8} + 4.47\times10^{-22}E^{4.4}} \quad (10^{-16}\mathrm{cm}^2), \quad (3)$$

and similarly for charge transfer in collisions of proton with SiH_4,

$$\sigma_{CX} = \frac{3.93}{\sqrt{E} + 445E^{2.3}} + \frac{46.2}{E^{0.094} + 9.0\times10^{-6}E^{1.2} + 2.845\times10^{-18}E^{3.8} + 5.81\times10^{-22}E^{4.4}} \quad (10^{-16}\mathrm{cm}^2). \quad (4)$$

It is clearly illustrated in Fig. 2 how the two semi-empirical formulae somewhat over-estimate recently acquired data: measurement and calculation in case of CH_4, and present theoretical results in case of SiH_4, in which case the current discrepancy varies between a factor of two and order of magnitude within the energy region considered. The shape of the cross section for plasma simulations is probably reasonable, given the scale of the neglect of other symmetries and collision configurations; however, much faster decay of the cross section is expected beyond 10 keV.

4. Summary

We have presented a brief summary of recently available cross sections for charge transfer in collisions of proton with methane, and provided the first calculated results for charge transfer in collision of proton with silane, using the approximation of equilibrium geometry and C_{3v} point-group projected potential energy surface. The comparison to semi-empirical formulae from the Juelich report on plasma simulation confirms reasonable agreement in the shape of cross section between 200 eV and 2 keV, but indicates that amendments of the functional form may be in place to achieve quantitative accuracy with respect to the recent measurements and present calculations. This is especially important in case of the Silane target, for which reliable cross section results are scarce. It may indeed be a worthwhile effort to calibrate the available charge transfer cross sections with respect to the ionization potential across a group of molecular targets to obtain better interpolation results, which has been recently proposed by Imai *et al*. [13].

Acknowledgments

Financial support by Ministry of Education is hereby gratefully acknowledged. This work was performed with support of Collaborative Research Program of National Institute for Fusion Science.

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