The formation of SiH$^+$, PH$^+$, and SH$^+$ by radiative association

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Received July 19; accepted November 23, 1999

Abstract. Cross sections for the radiative association of Si$^+$, P$^+$, and S$^+$ with atomic hydrogen to form the diatomic molecular ions SiH$^+$, PH$^+$, and SH$^+$, respectively, are presented. The results are obtained using fully quantum-mechanical techniques and utilize ab initio molecular data calculated with the multireference single- and double-excitation configuration-interaction (MRD-CI) method. Thermal rate coefficients are presented and applications of the results to diffuse interstellar clouds are discussed.

Key words: molecular processes — ISM: molecules

1. Introduction

Molecule formation processes involving second-row elements are of considerable interest, as searches for new molecular species in a variety of interstellar and circumstellar environments continue. Phosphorus-, sulfur- and silicon-containing molecules have been observed and identified, but no diatomic hydrides of these elements, or their associated ions, have been detected to date (Millar & Hobbs 1988; Magnani & Salzer 1989, 1991). Other diatomic hydrides, such as OH (which is chemically similar to SH), and diatomic hydride ions, such as CH$^+$ (which is chemically similar to SiH$^+$) have been observed in considerable abundance. Among the formation mechanisms for SiH$^+$, PH$^+$, and SH$^+$, the process of radiative association should be included.

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Using ab initio molecular potential energy curves and transition moments, we have carried out calculations for the radiative association of X^+ (X = Si, P, or S) with H:

$$X^+ + \mathrm{H} \rightarrow X\mathrm{H}^+ + \nu. \tag{1}$$

We present cross sections as a function of collision energy and give rate coefficients over a range of temperatures from 10 to 10 000 K. We compare our rates for radiative association of X^+ with H to other competing processes for the formation of $X\mathrm{H}^+$ in interstellar clouds.

2. Theoretical considerations

Because the population of the excited states of atoms is negligible in typical interstellar clouds, only molecular states correlating to the ground state of the separated atoms need be considered. The largest cross sections for direct radiative association result when X^+ and H approach along an excited state potential energy curve and then radiate via a strong dipole transition to the ground state (Babb & Kirby 1998). Transitions take place from the vibrational continuum of the excited state to the bound vibrational levels of the lower state. In this way, the molecules SiH$^+$ and PH$^+$ are formed through the $A\ ^1\Pi - X\ ^1\Sigma^+$ and the $1\ ^2\Sigma^- - X\ ^2\Pi$ transitions, respectively. In SiH$^+$, although the $1\ ^3\Sigma^+$ and the $a\ ^3\Pi$ states correlate also to the the ground state separated atom limit, the $1\ ^3\Sigma^+$ is repulsive enough that there is little overlap of its continuum wave functions with the bound vibrational wave functions in the $a\ ^3\Pi$ state (Sannigrahi et al. 1995). This same argument holds true for the $^4\Pi$ and $^4\Sigma^-$ states of PH$^+$ (Gu et al. 1999). Therefore, for both SiH$^+$ and PH$^+$, radiative association through these states of higher multiplicity will be negligible.

Table 1. Asymptotic separated-atom and united-atom limits

Molecular State	Separated-atom Atomic states	United-atom
SiH$^+$:		
$X\,^1\Sigma^+$	Si$^+$(3p ^{2}P$^\circ$) + H	3s^{2}3p^2 ^{1}D$_2$
$A\,^1\Pi$	Si$^+$(3p ^{2}P$^\circ$) + H	3s^{2}3p^2 ^{1}D$_2$
PH$^+$:		
$X\,^2\Pi$	P$^+$(3p^2 ^{3}P) + H	3s^{2}3p^3 ^{2} D$_J^o$
$1\,^2\Sigma^-$	P$^+$(3p^2 ^{3}P) + H	3s^{2}3p^3 ^{2} D$_J^o$
SH$^+$:		
$X\,^3\Sigma^-$	S$^+$(3p^3 ^{4}S$^\circ$) + H	3s^{2}3p^4 ^{3} P$_J$

For SH$^+$, only the $X\,^3\Sigma^-$ and $1\,^5\Sigma^-$ states correlate to ground state atoms. Dipole transitions are not allowed between these states, and the $1\,^5\Sigma^-$ is highly repulsive (Kimura et al. 1997), so radiative association can only occur within the $X\,^3\Sigma^-$ state itself, driven by the first and higher order derivatives of the $X\,^3\Sigma^-$ dipole moment function. As will be seen in Sect. 4, the cross sections for this latter process are much smaller than for the two-state process.

The radiative association cross section is given quantum mechanically by (cf. Zygelman & Dalgarno 1990; Babb & Kirby 1998)

$$\sigma(E) = \sum_{N'} \sum_{v''} \sigma_{N'}(v'', E), \qquad (2)$$

where

$$\begin{aligned}
\sigma_{N'}(v'', E) = \ & \tfrac{64}{3}\tfrac{\pi^5}{c^3}\tfrac{\nu^3}{k^2}p[S_{N'-1,N'}M^2_{v'',N'-1;k,N'} \\
& + S_{N',N'}M^2_{v'',N';k,N'} \\
& + S_{N'+1,N'}M^2_{v'',N'+1;k,N'}]. \qquad (3)
\end{aligned}$$

In Eq. (3), E is the relative collision energy, ν is the photon frequency, k is the wave number of relative motion, p is the probability of approach in the initial electronic state, N' is the initial rotational quantum number, v'' is the final vibrational quantum number, S is the Hönl-London factor, and M is the electric dipole matrix element connecting the initial and final nuclear and electronic states. The probability p for SiH$^+$, PH$^+$, and SH$^+$ is respectively $\tfrac{1}{6}$, $\tfrac{1}{9}$, and $\tfrac{3}{8}$ according to the degeneracy of the molecular state correlating to the relevant separated atom limits.

3. Potential curves and transition moments

The potential curves and electric dipole transition moments are calculated by the multireference single- and double-excitation (MRD-CI) configuration interaction method (Buenker & Peyerimhoff 1974, 1975; Buenker 1986), with configuration selection and energy extrapolation using the Table CI algorithm (Buenker 1980, 1981; Buenker & Phillips 1985). During the CI excitation procedure, the five lowest molecular orbitals

corresponding to 1s, 2s, and 2p orbitals of the heavy atoms are always doubly occupied, whereas some high virtual orbitals are discarded. The atomic orbital basis sets used in the present calculations contain at least one f-type function for the heavy atoms and one d-type function for the hydrogen atom. The basis sets consist of 73 contracted Gaussian functions for both PH$^+$ and SH$^+$, and 109 contracted functions for SiH$^+$. Further details about our MRD-CI calculations on these species can be found in the following references: for SiH$^+$ see Sannigrahi et al. (1995), for SH$^+$ see Kimura et al. (1997), and for PH$^+$ see Gu et al. (1999).

The potential curves of relevant states of the three ions are shown in Figs. 1 to 3, respectively. In the region $R \geq 2.0\ a_0$, the potentials are obtained from the ab initio calculations, whereas the potentials for $R < 2.0$ a_0 are obtained by fitting the last few ab initio points using the form $a\exp(-bR) + c$. The asymptotic separated-atom and united-atom limits of these states can be found in Table 1. The electric dipole and transition moments are shown in Fig. 4. In the short R region ($R < 2.0\ a_0$), their curves (full lines) are obtained by extrapolating the form $aR^2 + bR$ to zero at the united-atom limit by using the last few ab initio points. The contributions of the transition moments in the very short R region to the final cross sections are expected to be quite small although the exact positions of the "turning point" of the electric transition moments of PH$^+$ and SiH$^+$ are somewhat uncertain. Further details on SiH$^+$ are given in Stancil et al. (1997).

In Table 2, the spectroscopic constants, R_e (equilibrium distance), D_e and D_0 (dissociation energies), and ω_e (vibrational frequency), of the ground states for the three ions are listed together with previous experimental and theoretical results. It can be seen that there is generally good agreement between the present calculations and previous results. We find that the ground states of SiH$^+$, PH$^+$, and SH$^+$ support 22, 22, and 21 vibrational levels and 932, 760, and 731 rovibrational levels, respectively.

4. Results and discussion

Radiative association cross sections are shown in Fig. 5. Comparison of the cross sections for the three species clearly demonstrates the more favorable radiative association process for PH$^+$ and SiH$^+$, in which the two atomic species approach along an electronically excited state potential curve from which a dipole transition is made, than for SH$^+$, in which the entire process takes place within the ground electronic state. This difference is manifested by the two to three orders of magnitude difference in the cross sections. In addition, only the lowest energy region in the vibrational continuum of the SH$^+$ ground state contributes to the radiative association process, so the cross section drops off rapidly for collision energies greater

Table 2. Spectroscopic constants of the ground states

	R_e (a.u.)	D_e (eV)	D_0 (eV)	ω_e (cm^{-1})	References
SiH$^+$:					
This work	2.84	3.354	3.22	2155.0	
Exp.	2.842	3.354	3.22	2157.15	Carlson et al. (1980)
Exp.	2.842		3.17	2157.17	Huber & Herzberg (1979)
Theory	2.844		3.30	2161.23	Matos et al. (1988)
Theory	2.848	3.229		2155.35	Hirst (1986)
Theory	2.853		3.24	2153.5	Rosmus & Meyer (1977)
PH$^+$:					
This work	2.708	3.41	3.27	2370	
Exp.	2.693		3.34 ± 0.2	2299.6[a]	Narasimham (1957)
Theory	2.692	3.41	3.26	2354	Bruna et al. (1981)
Theory	2.704		3.31	2375.8	Rosmus & Meyer (1977)
SH$^+$:					
This work	2.581	3.52	3.36	2565	
Exp.	2.5772	(3.7)	(3.54)	2547.7	Rostas et al. (1984)
Theory	2.587	3.53	3.37	2535	Bruna et al. (1983)
					Hirsch & Bruna (1999)
Theory	2.585		3.73	2566.1	Rosmus & Meyer (1977)

[a] This value corresponds to $\Delta G_{1/2}$.
[b] Values in paratheses are estimates.
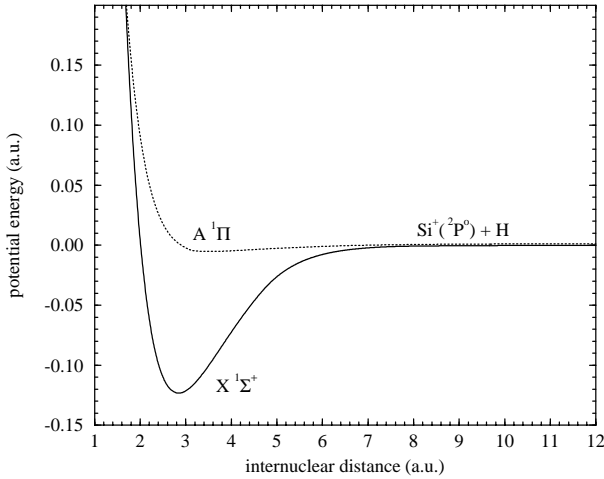
Fig. 1. The X $^1\Sigma^+$ and A $^1\Pi$ potentials of SiH$^+$
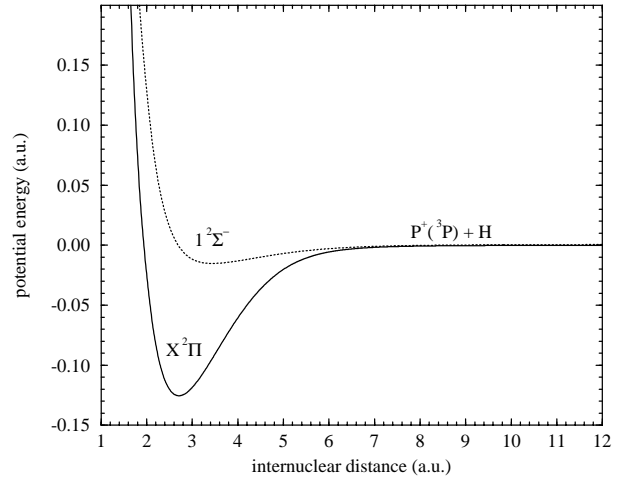
Fig. 2. The X $^2\Pi$ and 1 $^2\Sigma^-$ potentials of PH$^+$

than 0.1 eV. The larger cross section for SiH$^+$ relative to PH$^+$ can be understood by comparing the square of the dipole moments of these two species in the region 2 a.u. $< R <$ 3 a.u.

In Fig. 6 and Table 3, we present radiative association rate coefficients which were determined by averaging over the cross sections with a Maxwellian velocity distribution. The rate coefficients are fitted to the parametric form

$$\alpha(T) = \sum_i a_i \left(\frac{T}{300}\right)^{b_i} \exp\left(\frac{-T}{c_i}\right) \qquad (4)$$

with the parameters a_i (cm^3 s^{-1}), b_i, and c_i (K) given at the bottom of Table 3. The fits deviate from the computed rate coefficients by less than 20%.
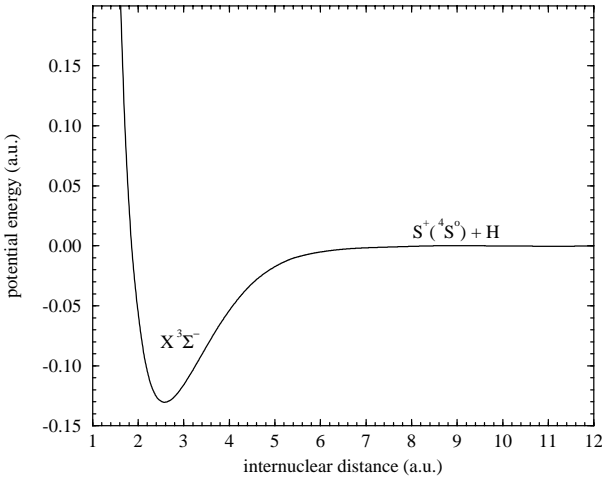
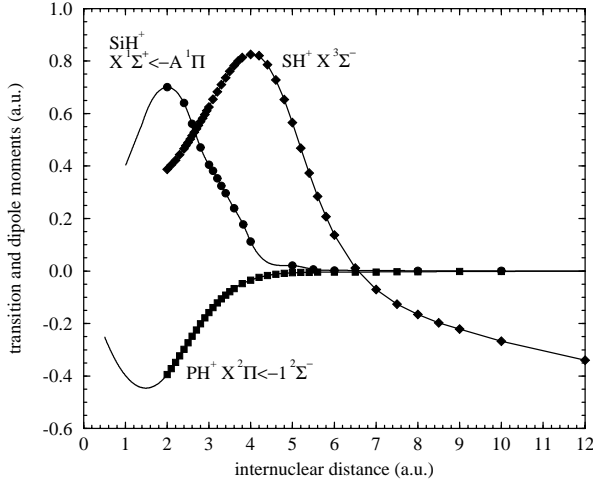**Fig. 3.** The X $^3\Sigma^-$ potential of SH$^+$

Fig. 5. Radiative association cross sections

Fig. 4. Transition moments of SiH$^+$ and PH$^+$ and the dipole moment of SH$^+$

Fig. 6. Radiative association rate coefficients

5. Astrophysical applications

In the diffuse interstellar medium phosphorus, sulfur, and silicon, with ionization potentials of 11.0, 10.36, and 8.15 eV, respectively, exist primarily as ions. The radiative association process may become significant in diffuse clouds and possibly translucent clouds and shocked regions, as the ratio of [H]/[H$_2$] increases. Other competing processes in the formation of "XH$^+$" are

$$X + H_3^+ \rightarrow XH^+ + H_2 \tag{5}$$

and

$$X^+ + H_2 \rightarrow XH^+ + H. \tag{6}$$

The latter reaction is usually endothermic.

In Fig. 7 we compare the present calculations of the rate coefficient for formation of SiH$^+$ with a prediction

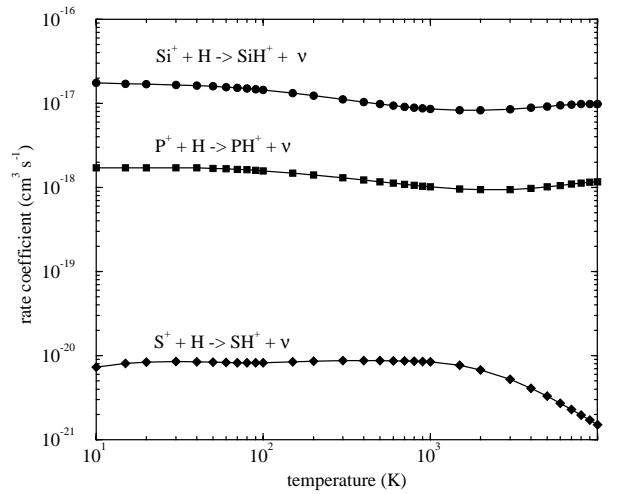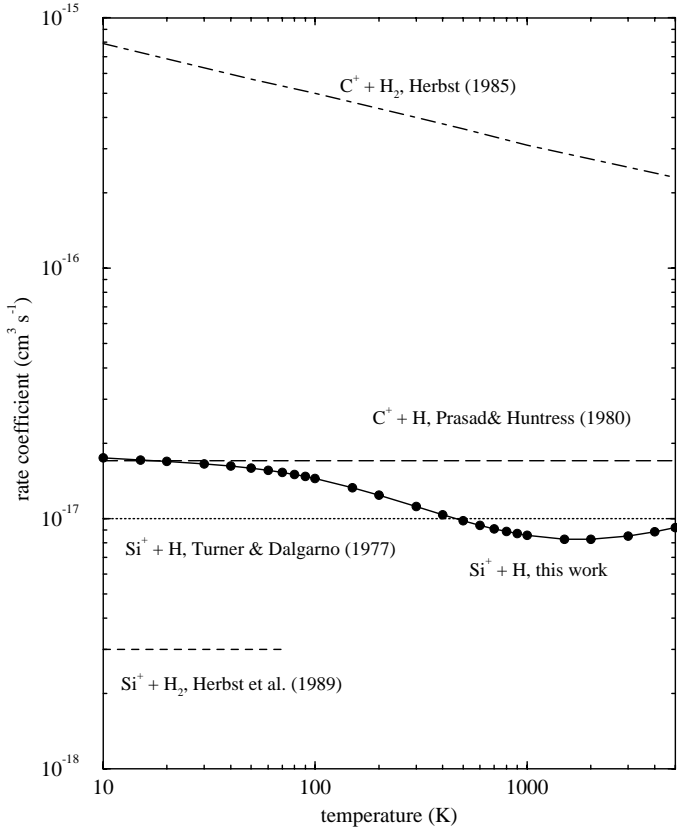for the radiative association of Si$^+$ with H$_2$ (Herbst et al. 1989), and with equivalent mechanisms for forming the chemically similar molecule CH$^+$. At low temperatures, our rate coefficients are a factor of two larger than the estimates of Turner & Dalgarno (1977), and are almost an order of magnitude larger than the radiative association rate coefficients of Si$^+$ with molecular hydrogen suggesting that the radiative association with atomic hydrogen will be the initiating reaction for the silicon chemistry when [H]/[H$_2$] > 0.1. At low temperatures, the C$^+$ and Si$^+$ radiative association rates appear to be comparable.

Rate coefficients for SH$^+$ and PH$^+$ from this work are plotted together with other reaction rates for S$^+$ and P$^+$ with H$_2$ in Fig. 8. For temperatures below about 500 K, radiative association of S$^+$ and P$^+$ with H appears to be

Table 3. Radiative association rate coefficients α (cm^3 s^{-1}) and fit coefficients for Eq. (4)

T(K)	Si$^+$ + H	P$^+$ + H	S$^+$ + H
10	1.75–17	1.70–18	7.32–21
20	1.69–17	1.71–18	8.35–21
50	1.59–17	1.69–18	8.34–21
80	1.50–17	1.62–18	8.20–21
100	1.45–17	1.58–18	8.22–21
200	1.24–17	1.41–18	8.58–21
500	9.79–18	1.17–18	8.70–21
800	8.88–18	1.06–18	8.58–21
1000	8.58–18	1.02–18	8.41–21
2000	8.26–18	9.40–19	6.78–21
5000	9.21–18	1.02–18	3.30–21
10000	9.84–18	1.17–18	1.50–21
a_1	1.07–17	1.22–18	9.25–21
b_1	–1.83–1	–1.46–1	5.60–2
c_1	–1.63+4	–2.14+5	5.27+3

Fig. 8. Comparison of the P$^+$ + H and S$^+$ + H reactions with other P$^+$ and S$^+$ reactions from Millar et al. (1997)

approximately one to three orders of magnitude smaller than that predicted with H$_2$.

In dense clouds, where almost all the hydrogen exists as H$_2$, P, S, and Si may be significantly depleted from the gas phase onto grain surfaces. In such regions, the presence of molecules containing these second-row elements may have more to do with grain disruption processes than with gas-phase chemistry.

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Fig. 7. Comparison with the Si$^+$ + H reaction with other Si$^+$ and C$^+$ reactions

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