THE RADIATIVE ASSOCIATION OF C AND S, C⁺ AND S, Si AND O, AND Si⁺ AND O

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ABSTRACT

Rate coefficients for radiative association of carbon and sulfur atoms to form CS, carbon ions and sulfur atoms to form CS^+, silicon and oxygen atoms to form SiO, and silicon ions and oxygen atoms to form SiO^+ are estimated for temperatures ranging from 300 to 14,700 K. For this temperature range, radiative association rate coefficients (k) are found to vary with temperature (T) as $k_{CS} = 4.36 \times 10^{-19} \, T^{0.22 \pm 0.01}$ cm³ s⁻¹ for CS, $k_{CS^+} = 3.07 \times 10^{-19} \, T^{0.15 \pm 0.02}$ cm³ s⁻¹ for CS^+, $k_{SiO} = 5.52 \times 10^{-18} \, T^{0.31 \pm 0.02}$ cm³ s⁻¹ for SiO, and $k_{SiO^+} = 6.22 \times 10^{-18} - 4.61 \times 10^{-22} \, T + 2.73 \times 10^{-26} \, T^2$ cm³ s⁻¹ for SiO^+. Our calculated rate coefficients k_{SiO} are higher than the values used in modeling the chemistry of SN 1987A and molecular outflow regions. On the other hand, for Si^+ and O, the rate coefficients are one order of magnitude lower than the values used in modeling the chemistry of circumstellar envelopes.

Subject headings: ISM: molecules — molecular processes

1. INTRODUCTION

Carbon monosulfide (CS) has been detected in several dense clouds (Hasegawa et al. 1984; Hayashi et al. 1985; Bachiller, Martín-Pintado, & Fuente 1991; Hauschildt et al. 1993), diffuse clouds (Drdla, Knapp, & van Dishoeck 1989), star-forming regions (Walker et al. 1986), carbon-rich stars (Bregman, Goebel, & Strecker 1978), circumstellar envelopes (Lindqvist et al. 1988; Omont et al. 1993), shocked molecular gas associated with the supernova remnant IC 443 (van Dishoeck, Jansen, & Phillips 1993), and comets (Smith, Stecher, & Casswell 1980; Jackson et al. 1982). These observations reveal that CS is present in a variety of astrophysical environments.

The carbon monosulfide ion (CS^+) has not been detected so far in the interstellar medium; however, steady state chemical models (Drdla et al. 1989; Mitchell, Ginsburg, & Kuntz 1978) have argued for the low abundance of the CS^+ ion in interstellar clouds. The formation of the CS^+ ion in interstellar clouds has been discussed by Quarta & Singh (1981) on the basis of ion-molecule reactions, charge transfer, photoionization, and radiative association processes, and predictions of finding the CS^+ ion at wavelengths near 5.8 mm, 7.3 μm, and 6702 Å have been made by them. Horani & Vervloet (1992) have studied the $CS^+(A\,^2\Pi_i - X\,^2\Sigma^+)$ transition by Fourier transform spectroscopy and have listed infrared transitions for the (1–0) band near 7.3 μm and microwave transitions $J = 0.5$–0.5 and $J = 1.5$–0.5 in the $v = 0$ level of the $X\,^2\Sigma^+$ state at 51.2210 ± 0.0035 GHz and 55.1165 ± 0.0050 GHz, respectively, in order to aid detection of the CS^+ ion in astrophysical objects. Unsuccessful attempts have been made in the search for the CS^+ ion at 6702 Å in the diffuse interstellar clouds in the ζ Oph and δ Sco lines of sight by Ferlet et al. (1983) and at 6840 Å toward the two lines of sight, ζ Oph and ζ Per, by Ferlet et al. (1986). Based on the level of detection of 0.03 mÅ for ζ Oph and 0.2 mÅ for ζ Per, Ferlet et al. (1986) have fixed the

upper limit of the CS^+ column densities $\leq 1.9 \times 10^{11}$ cm⁻² and $\leq 1.2 \times 10^{12}$ cm⁻² toward the ζ Ophiuchi and ζ Persei clouds, respectively. Assuming a 2 μs radiative lifetime of the $A\,^2\Pi_i$ state of the CS^+ ion and neglecting the variation of electronic transition moment (R_e) with internuclear distance (R), Quarta & Singh (1981) have estimated oscillator strengths ($f_{v'v''}$) of the $v'' = 0$ progression bands of the $CS^+(A\,^2\Pi_i - X\,^2\Sigma^+)$ transition. Using complete active space (CAS) self-consistent field (SCF) wavefunctions, Larsson (1985) has calculated $f_{v'v''}$ for electronic bands of $CS^+(A\,^2\Pi_i - X\,^2\Sigma^+)$, where the variation of R_e with R has been taken into account. With the $f_{v'v''}$ values of Larsson (1985), the upper limits of the predicted equivalent widths derived from equation (27) of Quarta & Singh (1981), the electronic bands (3, 0), (2, 0), and (4, 0) would be 0.1 mÅ, 0.1 mÅ, and 0.09 mÅ for clouds with hydrogen densities $n(H) + 2n(H_2) = 10$ cm⁻³ (Mitchell et al. 1978). For clouds with hydrogen densities > 10 cm⁻³ (Mitchell et al. 1978), these upper limits would be much lower.

Silicon monoxide has been detected in the spectra of SN 1987A (Aitken et al. 1988a, b; Roche, Aitken, & Smith 1993; Wooden et al. 1993; Bouchet, Danziger, & Lucy 1991), stellar atmospheres (Knacke et al. 1969; Beer, Lambert, & Sneden 1974; Olofsson et al. 1982), interstellar clouds (Wilson et al. 1971; Martín-Pintado, Bachiller, & Fuente 1992), regions with high density and temperature associated with outflows from young stellar objects (Lada, Oppenheimer, & Hartquist 1978; Downes et al. 1982), and shocked clumps associated with the supernova remnant IC 443 (Ziurys, Snell, & Dickman 1989b; van Dishoeck et al. 1993). The SiO abundances in hot and shocked gas are larger than those in the cold quiescent gas by two or more orders of magnitude (Bachiller et al. 1991; Martín-Pintado et al. 1992; van Dishoeck et al. 1993). Recent observations of SiO in emission toward several molecular clouds (Ziurys, Friberg, & Irvine 1989a) show that the abundance ratio SiO/HCN is strongly dependent on the kinetic temperature of the regions.

The SiO^+ ion has been included in the silicon chemistry proposed for interstellar clouds by Turner & Dalgarno (1977) and Langer & Glassgold (1990), shocked regions by Hartquist, Oppenheimer, & Dalgarno (1980) and Neufeld & Dalgarno

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(1989), and circumstellar shells by Scalo & Slavsky (1980) and Clegg, van Ijzendoorn, & Allamandola (1983). Lovas (1974) has suggested SiO$^+$ as a possible source of the radio line U86.2 detected by Snyder & Buhl (1974) in the direction of the Orion Nebula molecular cloud. Recently, Zhang et al. (1993) have studied the (0, 0) and (1, 0) bands of the SiO$^+$ ($B\,^2E^+$–$X\,^2\Sigma^+$) transition at very high resolution and have concluded that SiO$^+$ is an unlikely candidate for the radio line U86.2 measured at 86,243.45(40) MHz by Snyder & Buhl (1974). Probably the U86.2 line originates from the $v = 1$, $J = 2 \rightarrow 1$ transition in SiO (Lovas 1974; Engels & Heske, 1989).

The radiative association process plays an important role in the formation of simple molecules found in supernovae (Liu & Dalgarno 1994), stellar atmospheres (Scalo & Slavsky 1980; Clegg et al. 1983; Langer & Glassgold 1990), interstellar clouds (Bates 1987; Herbst & Bates 1988), and molecular outflow regions (Glassgold, Mamon, & Huggins 1991). Liu & Dalgarno (1994) have modeled the chemistry of SiO in SN 1987A and have proposed the radiative association reaction.

$$\text{Si} + \text{O} \rightarrow \text{SiO} + h\nu \qquad (1)$$
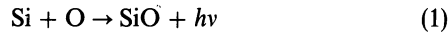
as the formation mechanism of SiO in SN 1987A. Because the rate coefficient scales as the cube of the transition frequency, Liu & Dalgarno (1994) have adopted a rate coefficient of 2×10^{-18} cm^3 s^{-1} for reaction (1), which is an order of magnitude smaller than the corresponding rate coefficient for the C + O reaction (Dalgarno, Du, & You 1990). Other adopted values for k_{SiO} are 1×10^{-17} cm^3 s^{-1} and 2×10^{-17} cm^3 s^{-1} by Clegg et al. (1983) and Glassgold et al. (1991), respectively, in their theoretical models. For the radiative association of Si$^+$ and O atoms

$$\text{Si}^+ + \text{O} \rightarrow \text{SiO}^+ + h\nu \qquad (2)$$
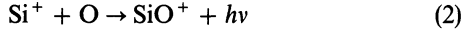
to form SiO$^+$, a value of 1×10^{-17} cm^3 s^{-1} has been estimated by Clegg et al. (1983) for circumstellar silicon chemistry of O-rich red giant stars. Glassgold et al. (1991), by analogy with carbon, have adopted 2×10^{-18} cm^3 s^{-1} in their theoretical model for the radiative association rate coefficient ($k_{\text{SiO}+}$) of SiO$^+$ in the cooler part of the protostellar winds where other formation mechanisms of molecules are inoperative. In this paper we present theoretical estimates of radiative association rate coefficients for carbon and sulfur atoms to form CS, carbon ions and sulfur atoms to form the CS$^+$ ion, silicon and oxygen atoms to form SiO, and silicon ions and oxygen atoms to form the SiO$^+$ ion for temperatures ranging from 300 to 14,700 K.

2. RADIATIVE ASSOCIATION

Many methods are available for estimating rate coefficients of radiative association reactions (Bates 1951; Zygelman & Dalgarno 1988). For collisions of heavy species, the rate coefficient $\alpha(T)$ at a temperature T (Zygelman & Dalgarno 1988) is given by

$$\alpha(T) = \left(\frac{8}{\mu\pi}\right)^{1/2} \left(\frac{1}{KT}\right)^{3/2} \int_0^\infty E\sigma(E) \exp\left(-\frac{E}{KT}\right) dE . \qquad (3)$$

In equation (3), $\sigma(E)$ is the collision cross section at an energy E of relative motion of two species

$$\sigma(E) = \sum_{\Lambda^u S} P_{\Lambda^u S} \sigma_{\Lambda^u S}(E) , \qquad (4)$$

where

$$\sigma_{\Lambda^u S}(E) = 4\pi \left(\frac{\mu}{2E}\right)^{1/2}$$

$$\times \int_0^\infty b\, db \int_{R_c}^\infty \left\{ A(R) \Big/ \left[1 - \frac{V_{\Lambda^u S}(R)}{E} - \frac{b^2}{R^2} \right]^{1/2} \right\} dR , \qquad (5)$$

μ is the reduced mass of the colliding particles in units of the electron's mass, b is the impact parameter, R_c is the distance of closest approach, and $V_{\Lambda^u S}$ is the molecular potential energy curve through which the colliding particles unite. $A(R)$ is the probability of radiative decay from an excited electronic state formed through bringing colliding particles together to a lower electronic state and is given by

$$A(R) = 2.03 \times 10^{-6} \frac{(2S + 1)(2 - \delta_{0,\Lambda^u + \Lambda^l})}{(2S + 1)(2 - \delta_{0,\Lambda^u})} |v(R)|^3 |D(R)|^2 , \qquad (6)$$

where $v(R)$ is the transition frequency at R in cm^{-1}; $D(R)$ is the electric dipole transition moment of electronic transition in atomic units; and Λ^u and Λ^l are components of the electronic orbital angular momentum of the upper and lower electronic states, respectively, along the internuclear axis of the formed molecule. The selection rules for strong electric dipole transitions are $\pm - \pm$, $\Delta S = 0$, and $\Delta\Lambda = 0, \pm 1$. In practice, weak transitions for which $\Delta S = \pm 1$ are readily observed for heavy species (Gaydon 1968, p. 52). Herbst & Bates (1988) and Bates (1987) have proposed that radiative association is considerably accelerated in situations in which one or more excited electronic states exist with potential minima lower than the dissociation limit of the ground state. The $P_{\Lambda^u S}$ in equation (4) is given by

$$P_{\Lambda^u S} = \frac{(2S + 1)(2 - \delta_{0,\Lambda^u})}{(2L_a + 1)(2S_a + 1)(2L_b + 1)(2S_b + 1)} . \qquad (7)$$

In equation (7), S is the resulting spin of the molecular state formed when two atoms with spins S_a and S_b are brought together, and L_a and L_b are orbital angular momenta of atoms a and b, respectively. At a given internuclear distance R, the probability of a radiative transition from an initially excited state is proportional to the cube of the transition frequency and the square of the electronic transition moment (see eq. [6]) involved in the radiative association process. Radiative transition probabilities fall off rapidly as R tends to infinity. Hence, radiative association of a pair of atoms is most likely to occur through an attractive potential along which the colliding atoms can penetrate to small distances.

2.1. Carbon Monosulfide (CS)

The approach of carbon (^3P) and sulfur (^3P) atoms, both in their ground state, would result in CS molecular electronic states Δ, $\Pi(2)$, $\Sigma^+(2)$, and Σ^-, each of multiplicities quintet, triplet, and singlet. The ground electronic state of CS is $X\,^1\Sigma^+$ (Bergeman & Cossart 1981), and according to the selection rules listed above strong electric dipole transitions to the $X\,^1\Sigma^+$ state can occur from two $^1\Pi$ and one $^1\Sigma^+$ molecular electronic states of CS. Among these, laboratory emission bands associated with the $A'\,^1\Sigma^+$–$X\,^1\Sigma^+$ transition (1700–2400 Å) have been observed in a microwave discharge by Bell,

Ng, & Suggitt (1972), and an extensive study of absorption and emission bands of the strong $A\,^1\Pi$–$X\,^1\Sigma^+$ system (2500–3100 Å) has been made in the laboratory by Bergeman & Cossart (1981). CI potential energy curves of $X\,^1\Sigma^+$, $A\,^1\Pi$, and $A'\,^1\Sigma^+$ states of CS have been calculated by Robbe & Schamps (1976), and, using the high-frequency deflection technique, the lifetimes of the $v' = 0$–5 levels of the CS $A\,^1\Pi$ state have been measured at high spectral resolution by Carlson et al. (1979). No lifetime measurement exists for the CS $A'\,^1\Sigma^+$ state. We have calculated the radiative association of $C(^3P)$ and $S(^3P)$ atoms to form CS through the $A\,^1\Pi$ molecular state, which radiates strongly to the ground state $X\,^1\Sigma^+$ in about 225 ns (Carlson et al. 1979). Potential energy curves of the CS $A\,^1\Pi$ and CS $X\,^1\Sigma^+$ states have been modeled with the Hulbert-Hirschfelder function (1941) using relevant molecular constants extracted from Huber & Herzberg (1979). The linear variation of electronic transition moment R_e with r-centroid ($r_{v'v''}$) (Coxon, Marcoux, & Setser 1976; Carlson et al. 1979) for the CS ($A\,^1\Pi$–$X\,^1\Sigma^+$) bands has been scaled in order to satisfy the sum rule prescribed by Larsson (1983). The radiative association rate coefficients through the $A\,^1\Pi$ state for the CS molecule at temperatures ranging from 300 to 14,700 K are listed in Table 1. They are 1.24×10^{-18} cm^3 s^{-1} and 3.37×10^{-18} cm^3 s^{-1} for temperatures 300 K and 14,700 K, respectively. The rate coefficients k_{CS} increase with increasing T and k_{CS} can be expressed as

$$k_{CS} = 4.36 \times 10^{-19} T^{0.22 \pm 0.01} \text{ cm}^3 \text{ s}^{-1} \qquad (8)$$

for the temperature range between 300 and 14,700 K. We have no information of the existence of any hump in the excited electronic state $A\,^1\Pi$ of CS. The presence of a barrier in the $A\,^1\Pi$ state would result in lower radiative association rate coefficients for CS. A comparison of radiative association rate coefficients of CS (this work) with those of isovalent CO (Dalgarno et al. 1990) shows that (1) for $T \sim 300$ K, k_{CS} is larger than k_{CO}, and (2) for $T > 300$ K, k_{CS} is smaller than k_{CO}.

2.2. Carbon Monosulfide Ion (CS$^+$)

The ground states of C$^+$ ions and sulfur atoms are $^2P^0$ and ^3P, respectively, and they can form the CS$^+$ ion by approaching along the quartet and doublet molecular states of symmetries Σ^+, Σ^-(2), Π(2), and Δ. The ground electronic state of the CS$^+$ ion is $X\,^2\Sigma^+$, and electronic bands belonging to the strong electric dipole transition CS$^+(A\,^2\Pi_i$–$X\,^2\Sigma^+)$ have been observed in the laboratory by Gauyacq & Horani (1978). Ab initio potential energy curves of the $X\,^2\Sigma^+$, $A\,^2\Pi$, and $B\,^2\Sigma^+$ electronic states and electronic transition moments of the A–X, B–X, and B–A electronic transitions of the CS$^+$ ion have been studied by Larsson (1985). The ratios of electronic transition moments of CS$^+(A\,^2\Pi_i$–$X\,^2\Sigma^+)$ bands, derived from oscillator strengths of Larsson (1985), are consistent with the corresponding observed R_e ratios derived from Mizukami et al. (1985). The potential energy curve CS$^+$ $A\,^2\Pi$ crosses the CS$^+$ $X\,^2\Sigma^+$ state at $R \sim 3.5a_0$, and radiative association of C$^+$ and S atoms to form the CS$^+$ ion can occur through the $A\,^2\Pi_i$ and $X\,^2\Sigma^+$ states followed by strong dipole transitions to the $X\,^2\Sigma^+$ and $A\,^2\Pi_i$ states, respectively. We have used ab initio potential energy curves of the $A\,^2\Pi_i$ and $X\,^2\Sigma^+$ states of the CS$^+$ ion, and electric dipole transition moments for CS$^+(A\,^2\Pi_i$–$X\,^2\Sigma^+)$ transition of Larsson (1985) for calculation of radiative association rate coefficients (k_{CS+}) between C$^+$ and S atoms to form CS$^+$ for temperatures ranging from 300 to 14,700 K. Our calculated rate coefficients k_{CS+} are listed in Table 1. These rate coefficients are three to four orders of magnitude lower than the rough estimate made by Quarta & Singh (1981). Unlike isovalent k_{CO+} (Dalgarno et al. 1990), the rate coefficients k_{CS+} (Table 1) increase very slowly with increasing temperature and for $300 < T < 14,700$ (K) can be expressed as

$$k_{CS+} = 3.07 \times 10^{-19} T^{0.15 \pm 0.02} \text{ cm}^3 \text{ s}^{-1} . \qquad (9)$$

The rate coefficient k_{CS+} is almost independent of temperature for $T > 2000$ K. For $T < 300$ K, the rate coefficient k_{CS+} would be much smaller than 5×10^{-19} cm^3 s^{-1} (Table 1), and hence the radiative association of C$^+$ and S atoms to form the CS$^+$ ion would be very slow in interstellar clouds.

2.3. Silicon Monoxide (SiO)

The silicon and oxygen atoms have ground-state configurations ^3P and ^3P, respectively, and can form by direct approach quintet, triplet, and singlet molecular electronic states of symmetries Δ, Π(2), Σ^+(2), and Σ^-. The ground electronic state of the SiO molecule is $X\,^1\Sigma^+$ (Huber & Herzberg 1979) and, according to the theoretical study of Heil & Schaefer (1972), 10 bound molecular electronic states ($X\,^1\Sigma^+$, $C\,^1\Sigma^-$, $A\,^1\Pi$, $D\,^1\Delta$, $a\,^3\Sigma^+$, $e\,^3\Sigma^-$, $b\,^3\Pi$, $d\,^3\Delta$, $^5\Sigma^+$, and $^5\Pi$) dissociate into the ground states of the atoms Si(^3P) + O(^3P). Of these, all have been observed except for the quintets which lie at higher energies (Field, Lagerqvist, & Renhorn 1976; Heil & Schaefer 1972). The $E\,^1\Sigma^+$ state has been correlated to Si(^1D) + O(^1D) by Elander & Lagerqvist (1971) and Heil & Schaefer (1972). However, according to Wigner-Witmer (1932) correlation rules (Gaydon 1968, p. 52) two electronic states, each of symmetry $^1\Sigma^+$, must dissociate to ground-state atoms. This conflict has been resolved by Field et al. (1976) who have suggested that the

TABLE 1

RADIATIVE ASSOCIATION RATE COEFFICIENTS

T (K)	C-S	C$^+$-S	Si-O	Si$^+$-O
300......	1.24	0.541	2.87	6.89
700......	1.75	0.783	4.27	6.24
1100......	2.05	0.922	5.09	5.81
1500......	2.26	1.009	5.63	5.49
1900......	2.43	1.067	6.06	5.24
2300......	2.56	1.107	6.32	5.05
2700......	2.67	1.133	6.38	4.90
3500......	2.83	1.164	7.11	4.68
4300......	2.96	1.179	7.49	4.54
5100......	3.05	1.184	7.83	4.45
5900......	3.12	1.185	8.13	4.40
7100......	3.19	1.185	8.53	4.37
8300......	3.25	1.183	8.87	4.40
9100......	3.28	1.182	9.08	4.44
10300......	3.31	1.182	9.35	4.53
11100......	3.32	1.182	9.51	4.61
12300......	3.34	1.184	9.73	4.74
13100......	3.35	1.187	9.87	4.84
13900......	3.36	1.189	9.99	4.96
14700......	3.37	1.193	10.1	5.07

NOTE.—Rate coefficients for Si-O (through $A\,^1\Pi$ and $E\,^1\Sigma^+$ states—see text) and Si$^+$-O (through $A\,^2\Pi$ state) are in units of 10^{-17} cm^3 s^{-1} and 10^{-18} cm^3 s^{-1}, respectively. The rate coefficients, in units of 10^{-18} cm^3 s^{-1}, for C-S are through approach $A\,^1\Pi$ state and for C$^+$-S through $A\,^2\Pi$ state.

$E\,^1\Sigma^+$ state dissociates adiabatically over a potential energy maximum to the ground-state atoms. In a theoretical SCF + CI study of low-lying molecular potential energy curves of the SiO molecule, Langhoff & Arnold (1979) have found a barrier of greater than 0.5 eV with a maximum near 5 Bohr radii in the $E\,^1\Sigma^+$ state of SiO. The $C\,^1\Sigma^-$ electronic state of the SiO molecule crosses the inner limb of the $A\,^1\Pi$ state at 1.515 Å near the turning points of the $v = 1$ level of the $A\,^1\Pi$ and the $v = 8$ level of the $C\,^1\Sigma^-$ state (Field et al. 1976; Langhoff & Arnold 1979). The ground-state dissociation energy (D_0^0) of the SiO is 8.26 eV, and potential minima of $A\,^1\Pi$ and $E\,^1\Sigma^+$ lie at 5.31 and 6.55 eV, respectively (Huber & Herzberg 1979). If we follow Herbst & Bates (1988) for direct radiative association, and if we consider only those transitions which are permitted for strong electric dipole transitions, the radiative association of Si and O atoms is possible by approaching through molecular excited $A\,^1\Pi$ and $E\,^1\Sigma^+$ states of SiO. $A\,^1\Pi$ and $E\,^1\Sigma^+$ states of SiO radiate to the ground state $X\,^1\Sigma^+$ in times less than 20 and 10 ns, respectively (Langhoff & Arnold 1979). Among A–X and E–X electronic transitions, the A–X band system is the predominant band system observed in the spectrum of SiO molecule.

The potential energy curves of the $A\,^1\Pi$, $E\,^1\Sigma^+$, and $X\,^1\Sigma^+$ states and the transition dipole moments of the A–X and E–X systems of SiO have been calculated by Langhoff & Arnold (1979) by means of the SCF + CI method. Their calculated transition moments for the two systems of SiO in question are in excellent agreement with the experimental values obtained by Park (1978) and Park & Arnold (1978) and their SCF + CI curves are in good agreement with the corresponding RKR curves of SiO. Excited states RKR potential energy curves $^3\Pi$, $^3\Sigma^+$, $^3\Delta$, $^1\Delta$, $^1\Sigma^-$, and $^3\Sigma^-$ all lie close to the $A\,^1\Pi$ state (Field et al. 1976). Unlike CO, the $A\,^1\Pi$ molecular state of SiO does not appear to have any repulsive hump (Langhoff & Arnold 1979). We have used the Hulbert-Hirschfelder function (1941) for construction of $A\,^1\Pi$, $E\,^1\Sigma^+$, and $X\,^1\Sigma^+$ potential energy curves, where experimental values of D_e, $\omega_e x_e$, α_e, ω_e, B_e, and r_e of the concerned molecular states of SiO are taken from Huber & Herzberg (1979). These potential energy curves are in good agreement with RKR and SCF + CI curves (Langhoff & Arnold 1979; Field et al. 1976). For temperatures ranging from 300 to 14,700 K, the radiative association of Si(^3P) and O(^3P) atoms through the $A\,^1\Pi$ state of SiO followed by a downward transition to $X\,^1\Sigma^+$ is found to vary from 2.87×10^{-17} to 7.16×10^{-17} cm^3 s^{-1}. The Si(^3P) and O(^3P) atoms may also approach forming SiO through the excited $E\,^1\Sigma^+$ state followed by a downward transition to the $X\,^1\Sigma^+$ state. The $E\,^1\Sigma^+$ state of SiO appears to have a hump of 5800 K at $R = 5a_0$ (Langhoff & Arnold 1979). Because of the barrier to a close approach through $E\,^1\Sigma^+$, the rate coefficient diminishes rapidly at low temperatures. For temperatures 1500–14,700 K, the radiative association rate coefficients through $E\,^1\Sigma^+$ are found to increase rapidly from 6.60×10^{-20} to 2.96×10^{-17} cm^3 s^{-1} for SiO. In Table 1, we list rate coefficients for direct radiative association of Si and O atoms for the temperature range 300–14,700 K. These rate coefficients can be represented approximately by

$$k_{\rm SiO} = 5.52 \times 10^{-18} T^{0.31 \pm 0.02} \text{ cm}^3 \text{ s}^{-1} \tag{10}$$

for T lying between 300 and 14,700 K. Radiative association rate coefficients $k_{\rm SiO}$ (see Table 1) for low temperatures are higher than the corresponding radiative association rate coefficients for isovalent molecule CO (Dalgarno et al. 1990). This is

mainly because of the fact that the electronic state $A\,^1\Pi$ of CO possesses a barrier of 950 ± 150 cm^{-1} (Simmons, Bass, & Tilford 1969), and its isovalent molecule SiO shows no evidence of hump in its excited electronic state $A\,^1\Pi$ (Langhoff & Arnold 1979). In addition, the transition probability depends on cube of frequency and square of dipole moment involved in the transition. A comparison of these parameters for SiO and CO shows that the frequency of CO(A–X) is smaller than the corresponding frequency of SiO(A–X), and the transition moment of the CO(A–X) is smaller than the corresponding moment of SiO(A–X). For 1900 K and 3500 K, our calculated radiative association rate coefficients for Si and O atoms are 6.06×10^{-17} cm^3 s^{-1} and 7.11×10^{-17} cm^3 s^{-1}, respectively. The corresponding rate coefficients for CO are 1.53×10^{-17} cm^3 s^{-1} and 2.56×10^{-17} cm^3 s^{-1} (Dalgarno et al. 1990).

2.4. *Silicon Monoxide Ion* (SiO$^+$)

In laboratory studies, Woods (1943) observed a band system near 3840 Å and assigned it to the $B\,^2\Sigma^+$–$X\,^2\Sigma^+$ transition of the SiO$^+$ molecule; this was later confirmed by Ghosh, Van der Linde, & Verma (1979). The $B\,^2\Sigma^+$ state does not appear to dissociate into the ground states of silicon ions and oxygen atoms. Colbourn et al. (1978) have studied the vacuum ultraviolet photoelectron spectrum of the SiO($X\,^1\Sigma^+$) molecule and have determined vertical ionization potentials of 11.61, 12.19, and 14.80 eV, corresponding to ionization of the $X\,^2\Sigma^+$, $A\,^2\Pi$, and $B\,^2\Sigma^+$ states of SiO$^+$, respectively. Ab initio calculations of potential energy curves of SiO$^+$ made by Werner, Rosmus, & Grimm (1982) show that (1) the $A\,^2\Pi$ excited state of SiO$^+$ is embedded in the $X\,^2\Sigma^+$ ground state, (2) vibrational levels between $1 \le v \le 10$ of the $X\,^2\Sigma^+$ state decay radiatively into lower levels of the $A\,^2\Pi$ state, and (3) SiO$^+$ is an excellent IR emitter.

The union of Si$^+$($^2P^0$) and O(^3P) atoms, both in their ground states, results in quartet and doublet molecular electronic states of symmetries Σ^+, Σ^-(2), Π(2), and Δ. Direct radiative association of Si$^+$ and O atoms is possible through molecular states $A\,^2\Pi$ and $X\,^2\Sigma^+$ states followed by strong dipole transitions to the $X\,^2\Sigma^+$ and $A\,^2\Pi$ states, respectively. Werner et al. (1982) have calculated potential energy curves, electronic transition moments, radiative association probabilities, and radiative lifetimes for the $X\,^2\Sigma^+$ and $A\,^2\Pi$ states of SiO$^+$ by the multiconfiguration SCF method. Their calculations yield molecular constants for the $X\,^2\Sigma^+$ and $A\,^2\Pi$ states of SiO$^+$ that are in good agreement with those obtained by experiments (see Table 1 of Werner et al. 1982). It is worth noting that electronic transition moment functions are steeper and transition moments of SiO$^+$($A\,^2\Pi$–$X\,^2\Sigma^+$) are larger than those of isoelectronic CO$^+$($A\,^2\Pi$–$X\,^2\Sigma^+$) (see Fig. 7 of Werner et al. 1982). We have calculated RKR potential energy curves for the $A\,^2\Pi$ and $X\,^2\Sigma^+$ states of SiO$^+$ using molecular constants listed by Werner et al. (1982). These RKR curves were extrapolated to the asymptotic form $V(R) = -(\frac{1}{2})\alpha R^{-4}$ a.u., where $\alpha = 5.28a_0^3$ is the polarizability of atomic oxygen (Kelly 1966). Using electronic transition moments of SiO$^+$($A\,^2\Pi$–$X\,^2\Sigma^+$) from Werner et al. (1982) and our calculated RKR curves, direct radiative association rate coefficients of Si$^+$ and O atoms have been calculated through the $A\,^2\Pi$ state followed by radiative decay to the $X\,^2\Sigma^+$ ground state of SiO$^+$. These rate coefficients are listed in Table 1 and can be fitted to the relation

$$K_{\rm SiO^+} = a_0 + a_1 T + a_2 T^2, \tag{11}$$

where a_0, a_1, and a_2 are equal to $(6.22 \pm 0.1) \times 10^{-18}$ cm^3 s^{-1}, $(-4.61 \pm 0.3) \times 10^{-22}$ cm^3 s^{-1} K^{-1}, and $(2.73 \pm 0.2) \times 10^{-26}$ cm^3 s^{-1} K^{-2}, respectively. The rate coefficients are found to decrease from 6.89×10^{-18} cm^3 s^{-1} to 4.37×10^{-18} cm^3 s^{-1} for the temperature range 300–7100 K, and they increase from 4.34×10^{-18} cm^3 s^{-1} to 5.07×10^{-18} cm^3 s^{-1} for the temperature range 7500–14,700 K. For isovalent CO$^+$, the rate coefficients k_{CO^+} decrease with increase of temperature (see Table 1 of Dalgarno et al. 1990). Glassgold et al. (1991) have adopted a rate coefficient of 2×10^{-18} cm^3 s^{-1} for SiO$^+$ radi-ative association from a similar reaction with carbon. Their rate coefficient is a factor of ~ 2 smaller than our estimated rate coefficient at temperatures about 6000 K.

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