Radiative association of Ti and O atoms

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ABSTRACT

Rate coefficients for the radiative association of titanium and oxygen atoms to form the titanium monoxide (TiO) molecule are estimated. The radiative association of Ti(^{3}F) and O(^{3}P) atoms is dominated by an approach along the C$^3\Delta$ potential energy curve, accompanied by spontaneous emission into the X$^3\Delta$ ground state of TiO. For temperatures ranging from 300–14 000 K, the total rate coefficients are found to vary from 4.76×10^{-17} to 9.96×10^{-17} cm^3 s^{-1}, respectively.

Key words: atomic data – atomic processes – circumstellar matter – ISM: molecules.

1 INTRODUCTION

Optical and near-infrared studies of electronic transitions of titanium oxide (TiO) have shown that this species is present in the stellar photospheres of late-K to early-L dwarf stars. The TiO molecule is generally the main opacity contributor in the optical spectra of M stars. The TiO bands strengthen rapidly with advancing type until at least M8 and disappear around mid- to late-L types (e.g. Kirkpatrick 2005). Chemical equilibrium calculations suggest that TiO disappears from the spectra of the coolest dwarfs because it converts into TiO$_2$ or other Ti-bearing molecules (Burrows & Sharp 1999; Allard et al. 2001; Lodders 2002).

Absorption features due to TiO are also prominent in the optical spectra of cool evolved oxygen-rich stars (Merrill 1940). Reid & Goldston (2002) explored a possible relation between TiO formation and the light-curve shape of Mira variables (S and M types). According to them, titanium can go from mostly atomic to molecular form as the temperature of the extended photosphere of a Mira variable decreases from about 2000 to 1600 K, via the chemical reaction Ti + O $\rightleftharpoons$ TiO. Once TiO forms, it can absorb most of the optical light and produces a large change in the visual luminosity of Mira stars. At temperatures lower than 1600 K, dust can form and remove TiO from the gas phase, greatly reducing the visual opacity from TiO (e.g. Reid & Goldston 2002; Alexander et al. 2003). Indeed, titanium oxide (TiO$_2$) was extracted from primitive meteorites (Nittler & Alexander 1999; Nittler et al. 2005). On the basis of the isotopic compositions of most of these grains, the atmospheres of evolved stars are considered the most likely stellar sources, whereas the ejecta of stellar explosions have also been suggested as astronomical sources (Nittler & Alexander 1999; Nittler et al. 2005).

Historically, the formation of the TiO molecules in interstellar clouds has been discussed by Oppenheimer & Dalgarno (1977). They suggested that TiO could be formed by an associative ionization process Ti + O $\rightarrow$ TiO$^+$ + e and the ion–neutral reactions Ti$^+$ + O$_2$ $\rightarrow$ TiO$^+$ + O and Ti$^+$ + H$_2$O $\rightarrow$ TiO$^+$ + O, followed by metal (M) charge exchange TiO$^+$ + M $\rightarrow$ TiO + M$^+$, radiative recombination with electrons TiO$^+$ + e $\rightarrow$ TiO + $h\nu$ and neutralization on grains TiO$^+$ + grain $\rightarrow$ TiO + grain. The TiO would be destroyed by chemical reactions with C$^+$, He$^+$ and H$^+$. This study indicates that TiO should be detectable in millimetre waves. However, TiO has not been detected at millimetre wavelengths in stellar atmospheres or towards molecular clouds (Churchwell et al. 1980; Millar et al. 1987). The apparent absence of interstellar TiO has been attributed to the inefficiency of the associative ionization reaction and the highly efficient dissociative recombination process TiO$^+$ + e $\rightarrow$ Ti + O under the prevailing conditions of the interstellar medium, or it has been suggested that the majority of Ti atoms are locked up in dust-grain cores (Churchwell et al. 1980; Millar et al. 1987; Turner 1991; Petrie & Bohme 1994).

TiO is known to have a considerable impact on the structure of the stellar atmosphere (Jørgensen 1994). In spite of such considerable progress, little is known about the mechanism for the formation of TiO in astronomical sources and, within the set of all possible reactions, the rate coefficients for radiative association should be known. Then, using theoretical potential energy curves and transition dipole moments, we present estimates of the rate coefficients for the radiative association of Ti and O atoms (k_{TiO}) to form the TiO molecule for temperatures in the 300–14 000 K range.

2 METHOD OF CALCULATION

A semi-classical description of nuclear motion may be applied to collisions of massive reactants or strong stabilizing transitions (e.g. Zygelman & Dalgarno 1988; Latter & Black 1991; Dalgarno, Du & You 1990); this was first formulated correctly by Bates (1951).

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In this approximation, the cross-section at an energy E of the relative motion of two heavy atomic species is given by

$$\sigma(E) = \sum_{\Lambda^u S} P_{\Lambda^u S}\, \sigma_{\Lambda^u S}, \qquad (1)$$

where

$$\sigma_{\Lambda^u S} = 4\pi \left(\frac{\mu}{2E}\right)^{1/2} \int_0^\infty b\, \mathrm{d}b \int_{r_c}^\infty \frac{A(r)\, \mathrm{d}r}{[1 - \frac{V_{\Lambda^u S}(r)}{E} - \frac{b^2}{r^2}]^{1/2}}, \qquad (2)$$

in which μ is the reduced 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 transition probability for emission and is obtained by the expression

$$A(r) = 2.03 \times 10^{-6} \frac{(2 - \delta_{0,\Lambda^u + \Lambda^l})}{(2 - \delta_{0,\Lambda^u})} |\nu(r)|^3 |R_e(r)|^2 \text{ s}^{-1}, \qquad (3)$$

in which $\nu(r)$ is the transition frequency in terms of wavenumbers (cm^{-1}) at internuclear distance r, $(2 - \delta_{0,\Lambda^u + \Lambda^l})/(2 - \delta_{0,\Lambda^u})$ is the degeneracy factor, $R_e(r)$ is the electronic 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 molecule formed. $P_{\Lambda^u S}$ is the probability of approach along any particular molecular potential energy curve and is given by

$$P_{\Lambda^u S} = \frac{(2S + 1)(2 - \delta_{0,\Lambda^u})}{(2L_{Ti} + 1)(2S_{Ti} + 1)(2L_O + 1)(2S_O + 1)}, \qquad (4)$$

where, S_{Ti}, S_O, L_{Ti} and L_O are the electronic spin and electronic angular momenta of the titanium and oxygen atoms and S is the resulting spin of the molecular electronic state.

The rate coefficient $\gamma(T)$ at a temperature T for a Maxwellian velocity distribution is given by

$$k(T) = \left(\frac{8}{\mu\pi}\right)^{1/2} \left(\frac{1}{k_B T}\right)^{3/2} \int_0^\infty E\, \sigma(E) \exp\left(-\frac{E}{k_B T}\right) \mathrm{d}E, \qquad (5)$$

where k_B is the Boltzmann constant.

3 RADIATIVE ASSOCIATION

The coupling of Ti(^{3}F) and O(^{3}P) atoms, both in their ground state, results in singlet, triplet and quintet molecular electronic states of symmetries Γ, $\Phi(2)$, $\Delta(3)$, $\Pi(3)$, $\Sigma^+(2)$ and Σ^-. There are eight known singlet states (a$^1\Delta$, f$^1\Delta$, d$^1\Sigma^+$, c$^1\Phi$, b$^1\Pi$, h$^1\Sigma^+$, g$^1\Gamma$ and i$^1\Pi$) and seven triplet states (X$^3\Delta$, C$^3\Delta$, D$^3\Sigma^-$, A$^3\Phi$, A$^3\Pi$, B$^3\Pi$ and $^3\Sigma^+$) that dissociate into the ground state of Ti(^{3}F) and O(^{3}P) atoms (e.g. Miliordos & Mavridis 2010). Of these, all have been observed except for the g = $1^1\Gamma$, i = $2^1\Pi$, h = $2^1\Sigma^+$ and $1^3\Sigma^+$ states (Schwenke 1998; Dobrodey 2001). The dissociation energy of TiO has been confirmed to be $D_0 = 6.87 \pm 0.07$ eV (Naulin, Hedgecock & Costes 1997; Loock et al. 1998).

In early *ab initio* works, Carlson & Moser (1963) and Carlson & Nesbet (1964) have performed calculations on X$^3\Delta$, a$^1\Delta$ and d$^1\Sigma^+$ states of TiO at the Hartree–Fock level. 20 years later, Bauschlicher, Bagus & Nelin (1983) described the lowest states of TiO using complete active space self-consistent field (CASSCF) calculations. Bauschlicher, Langhoff & Komornicki (1990) examined the X$^3\Delta$, a$^1\Delta$, d$^1\Sigma^+$, A$^3\Phi$, E$^3\Pi$ and $^3\Sigma^-$ states of TiO at the CASSCF level of theory. Using state-average (SA)-CASSCF and internally contracted multireference configuration interaction (IC-MRCI) methods, Langhoff (1997) studied all the dipole-allowed transitions connecting the a$^1\Delta$, b$^1\Pi$, d$^1\Sigma^+$, c$^1\Phi$ and f$^1\Delta$ singlet states and the X$^3\Pi$, A$^3\Phi$, B$^3\Pi$, C$^3\Delta$ and E$^3\Pi$ triplet states.

Schwenke (1998) reported spectroscopic constants for 12 states of TiO with the SA-CASSCF approach. Dobrodey (2001) used the MRCI method to examine electronic transition moments and oscillator strengths, extending the work of Langhoff (1997) to 10 singlets and 10 triplet states of TiO. Other calculations on TiO, but only for five low-lying states, were reported by Kobayashi et al. (2002) using SA-CASSCF/IC-MRCI methods. Recently, Miliordos & Mavridis (2010) have constructed complete potential energy curves for a large number of states of TiO at the restricted coupled-cluster singlet doubles quasi-perturbative connected triplet (MRCI/RCCSD(T)) level.

Because of its astrophysical importance, the TiO molecule is the most investigated gas-phase transition metal oxide experimentally. A review of extensive spectroscopic data bases for the TiO molecule can be found in Amiot, Luc & Vetter (2002), Kobayashi et al. (2002) and Ram et al. (1999).

The adopted potential energy curves of singlet and triplet states have been modelled with the Hulbert–Hirschfelder function (Hulbert & Hirschfelder 1941, hereafter HH; Appendix A), using molecular constants extracted from several spectroscopic and *ab initio* studies. These constants are listed in Table 1 and the potential energy curves are depicted in Figs 1 and 2. For D$^3\Sigma^+$, g$^1\Gamma$, h$^1\Sigma^+$, i$^1\Pi$ and $1^3\Sigma^+$ states some spectroscopic constants are still missing and they were estimated from available data using some well-known relationships between these constants (Herzberg 1950).

The radiative association of Ti(^{3}F) and O(^{3}P) atoms is dominated by the approach along the C$^3\Delta$ potential energy curve accompanied by spontaneous emission into the X$^3\Delta$ ground state of TiO (Fig. 1). The probability of approach along the C$^3\Delta$ state is 6/189. The variation of the transition moment with internuclear distance was taken from Langhoff (1997) in the 2.5–3.6 a_0 range.

Table 1. Molecular constants for the electronic states of TiO.[a]

State	T_e	w_e	$w_e x_e$	B_e	α_e	r_e
X$^3\Delta$[b]	0.0	1009.18	4.562	0.5353	3.0237	1.6203
E$^3\Pi$[c]	11870.2	912.90	5.1	0.5167	3.235	1.6493
D$^3\Sigma^-$[d]	12284	968	5.369[e]	0.5105	3.62174[e]	1.659
A$^3\Phi$	14094.17[f]	867.52[b]	3.833[b]	0.5073[b]	3.1666[b]	1.6645[b]
B$^3\Pi$[g]	16219.18	865.88	0.9246	0.5076	3.17923	1.664
C$^3\Delta$[m]	19424.87	838.26	4.7592	0.4899	3.062	1.6938
$1^3\Sigma^+$[h]	20556	832	7.5	0.4772[e]	3.5	1.716
a$^1\Delta$	3443.28[i]	1018.27[j]	4.521[j]	0.5376[j]	2.916[j]	1.61674[j]
d$^1\Sigma^+$	5663.15[k]	1023.06[l]	4.8935[l]	0.5493[l]	3.3483[l]	1.600[m]
b$^1\Pi$	14717.19[k]	919.76[l]	4.2791[l]	0.5135[l]	2.839[l]	1.6546[m]
g$^1\Gamma$[n]	15810.09	931.08	3.83	0.5131	2.797	1.6548[e]
h$^1\Sigma^+$[n]	18596	913	4.6	0.5044[e]	3.12	1.670
c$^1\Phi$	21278.90[i]	917.55[m]	4.42[m]	0.5230[i]	3.411[e]	1.6393[i]
i$^1\Pi$[h]	22608	949	5.6	0.5044[e]	3.5	1.669
f$^1\Delta$	22513.36[k]	874.10[j]	2.50[j]	0.5038[j]	3.078[j]	1.670[j]

[a] Units are cm^{-1} and $\alpha_e(10^{-3}$ cm$^{-1})$, except r_e (Å).
[b] Ram et al. (1999).
[c] Kobayashi et al. (2002).
[d] Barnes, Merrer & Metha (1997).
[e] Estimated (see text).
[f] Barnes, Merrer & Metha (1996).
[g] Amiot et al. (2002).
[h] Miliordos & Mavridis (2010).
[i] Amiot et al. (1996).
[j] Brandes & Galehouse (1985).
[k] Kaledin, McCord & Heaven (1995).
[l] Galehouse, Brault & Davis (1980).
[m] Phillips (1973).
[n] Schwenke (1998).

Figure 1. Potential energy curves for the lowest lying triplet states of the TiO molecule.
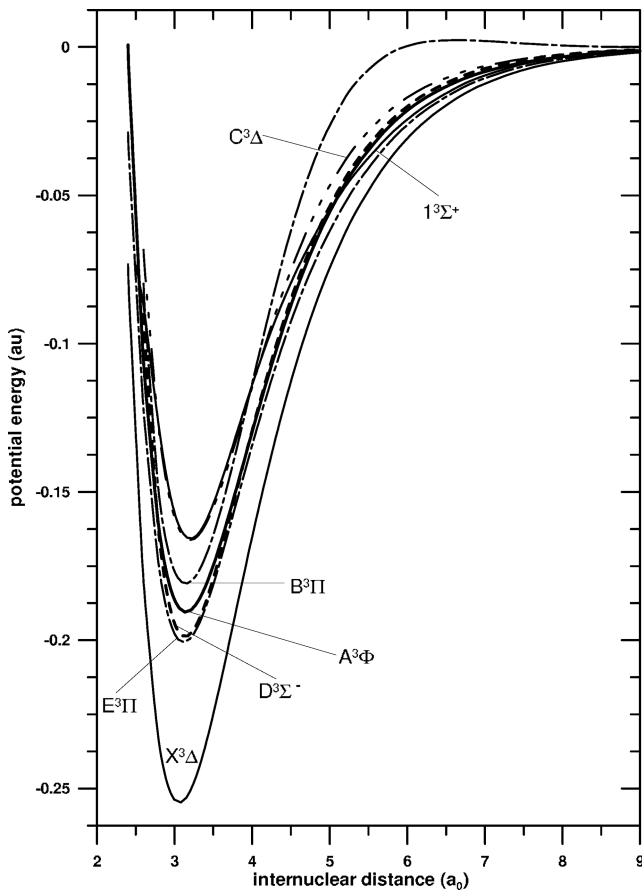

Figure 2. Potential energy curves for the lowest lying singlet states of the TiO molecule.

According to this author, the electronic transition moment functions for the systems of TiO are obtained over a large enough range of r values that no uncertainty is introduced into the calculated radiative lifetime, which is in agreement with the experiments (e.g. Kobayashi et al. 2002). However, for radiative association rate coefficient calculations, transition moments are needed over a large range of internuclear distances. At short range, the transition moments were extrapolated using a cubic spline and joined smoothly to the form $R_e(r) = 1.667607r - 0.388458r^2$ (Dalgarno, Kirby & Stancil 1996). At large separations, the function $R_e(r) = 31.882095 \exp(-0.984339r)$ was applied (Stancil & Dalgarno 1997). For temperatures ranging from 300–14 000 K, the coupling of the Ti and O atoms through the $C^3\Delta$ state of TiO followed by a downward transition to the $X^3\Delta$ state is found to vary from 2.31×10^{-17} to 4.00×10^{-17} cm^3 s^{-1} and this is depicted in Fig. 3.

Since the total rate coefficient is dominated by the C–X transition, it is interesting to compare the rate coefficient obtained with the theoretical $R_e(r)$ function with that measured experimentally by Namiki, Saitoh & Ito (2004). The measured $R_e(r)$ function was determined in the 1.62093–1.80255 Å range, which was used for calculation of the rate coefficient for the C–X transition. For small internuclear distances, the experimental transition dipole moments were extrapolated using the form $R_e(r) = 1.70345r - 0.41165r^2$. For large distances, the function $R_e(r) = 24.468453 \exp(-0.861721r)$ was used. The values of rate coefficients vary from 2.27×10^{-17} to 4.11×10^{-17} cm^3 s^{-1} for temperatures in the range 300–14 000 K, respectively, in good agreement with those obtained with the theoretical transition dipole moments of Langhoff (1997). In both cases,
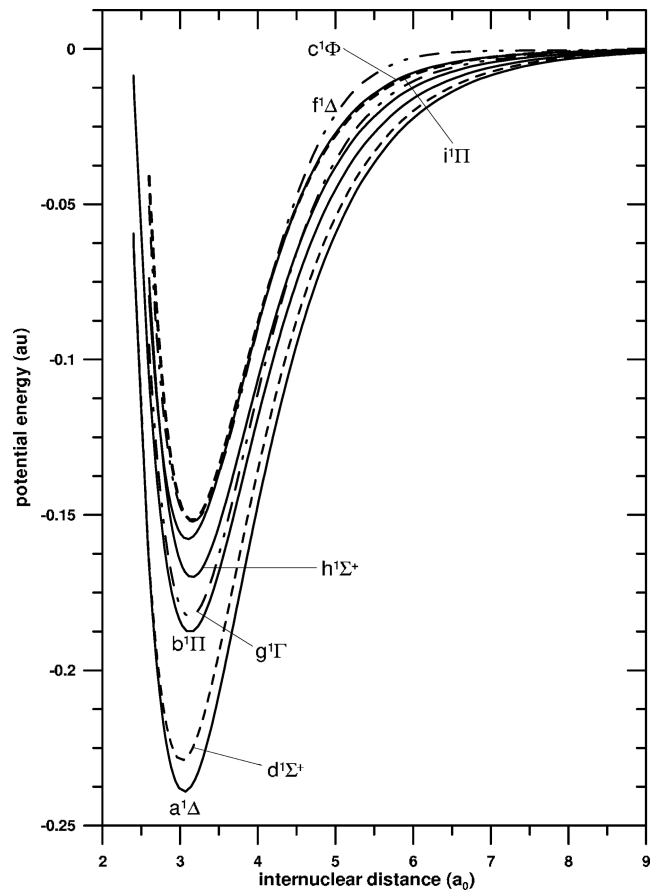
the dipole moments quickly fall to zero at large distances and the integration may be stopped around 5–5.5 a$_0$. Thus, it is expected that the dipole moments extrapolated do not introduce significant errors in the values of the calculated rate coefficients. However, because we do not take into account the fine structure of the titanium and oxygen atoms, our predicted rate coefficients are unreliable at low temperatures. The maximum values of the components of the fine structure of Ti and O atoms are 387 and 227 cm^{-1}, respectively. Hence, the maximum splitting in the asymptotic potentials is around 614 cm^{-1} or 883 K and considerable uncertainty is expected in rate coefficients below 1000 K. Moreover, the semi-classical method of Bates (1951) ignores quantum effects such as shape resonance. Antipov et al. (2009) have shown that this effect considerably increases the values of the rate coefficients of formation of the CN radical by radiative association at low temperatures, and even at moderate temperatures (1900 K) this effect is still relevant. However, the resonances are not as significant to CN as for light compounds containing hydrogen, such as HD, LiH or HeH$^+$ (e.g. Antipov et al. 2009). Thus, it is expected that the contribution of quantum resonance is not as significant for TiO as for CN, since TiO is a compound heavier than CN. Still, for CN, Antipov, Gustafsson & Nyman (2011) showed that HH potentials and *ab initio* potentials differ mainly at large internuclear distances and at low temperatures the function HH provides cross-sections substantially lower than those obtained with *ab initio* potentials. As mentioned, the integration for the C–X transition of TiO can be stopped around 5 a$_0$. Therefore it is expected that the HH function does not introduce large errors in the calculations of the rate coefficients of TiO.
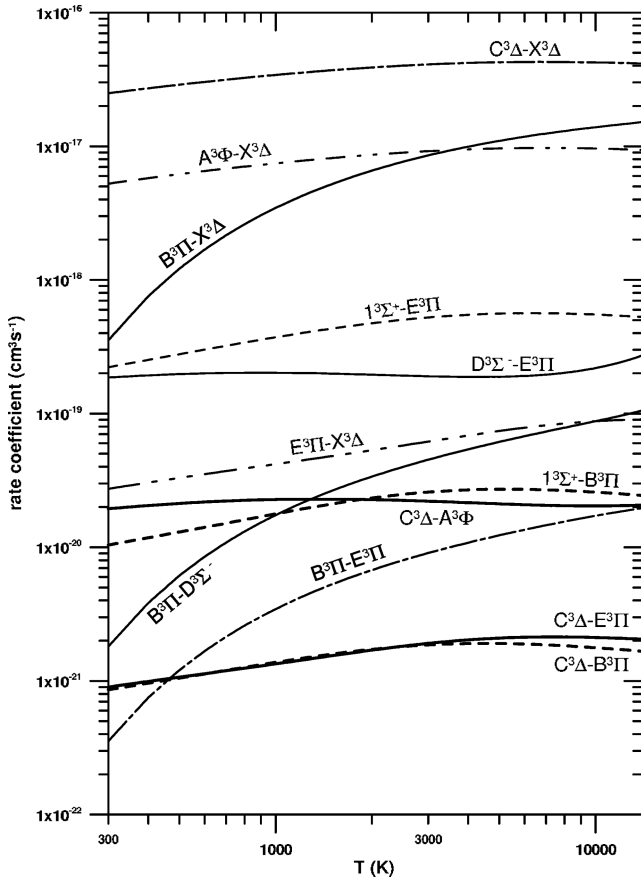
Figure 3. Rate coefficients for formation of TiO through triplet states.

Figure 4. Rate coefficients for formation of TiO through singlet states.

Considering all these effects, it is likely that an uncertainty of a factor of 2 is probably more dependable at low temperatures; for values higher than about 2000 K the rate coefficients are sufficiently accurate for most practical applications. However, these effects should be considered in future work to ensure accurate rate coefficients at low temperatures.

The rate coefficients for radiative association of the TiO molecule were also calculated through C–A, C–E, C–B, B–X, B–D, B–$^3\Sigma^+$, E–X, E–B, E–D, E–$^3\Sigma^+$ and A–X transitions. The probability of approach through the D$^3\Sigma^-$ and $1^3\Sigma^+$ states is 3/189 and that through the A$^3\Phi$, C$^3\Delta$, E$^3\Pi$ and B$^3\Pi$ states is 6/189. The variation of R_e with r for the C–A, C–B, C–E, E–X, E–B, B–X and A–X systems has been taken from Langhoff (1997). The corresponding variation for R_e with r for the E–D, E–$^3\Sigma^+$, B–D and B–$^3\Sigma^+$ systems has been extracted from Dobrodey (2001). The rate coefficients for approach along excited triplet states are displayed in the Fig. 3 for temperatures in the range 300–14 000 K. The values of the rate coefficient for the C–X transition are higher than those for the other transitions, consistent with the greater photon energy and considerably large transition dipole moments involved in the C–X transition. Additionally, the A–X dipole moments are rather large, as is the state separation; this channel makes an important contribution to the total rate coefficients. The HH B$^3\Pi$ potential energy curve exhibits a repulsive hump at a nuclear separation of ~6.8 a$_0$. Because of the barrier, the rate coefficient diminishes rapidly at low temperatures. The E–X transition possesses a relatively large state separation, but its dipole moments are extremely small. Thus, this transition contributes negligibly to radiative association. Finally, the C–E, C–A, C–B and B–E transition frequencies are relatively small, as are the
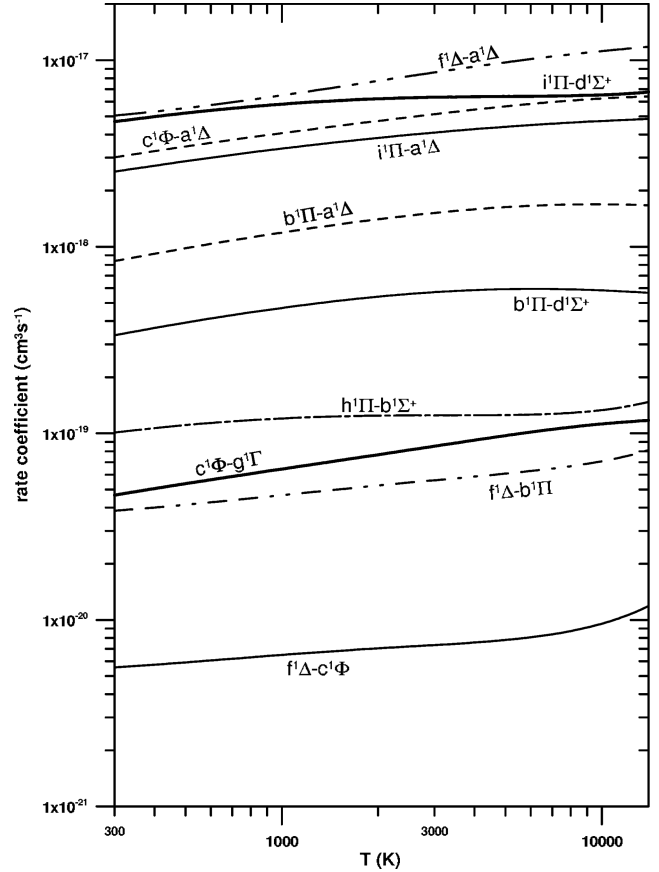
corresponding transition moment functions, so these four channels make a negligible contribution to the radiative association rate coefficients. The total rate coefficients for association through triplet states are found to vary from 3.10×10^{-17} to 6.72×10^{-17} cm^3 s^{-1} for temperatures ranging from 300–14 000 K, respectively.

Radiative association of Ti(^{3}F) and O(^{3}P) atoms can also occur following approach along the b$^1\Pi$, c$^1\Phi$, f$^1\Delta$, i$^1\Pi$, g$^1\Gamma$ and h$^1\Sigma^+$ states. There are also three channels for radiative decay of the f$^1\Delta$ state (f$^1\Delta$–a$^1\Delta$, f$^1\Delta$–c$^1\Phi$ and f$^1\Delta$–b$^1\Pi$ transitions), three channels for the b$^1\Pi$ state (b$^1\Pi$–a$^1\Delta$, b$^1\Pi$–h$^1\Sigma^+$ and b$^1\Pi$–d$^1\Sigma^+$ transitions) and two channels for both c$^1\Delta$ state (c$^1\Delta$–a$^1\Delta$ and c$^1\Delta$–g$^1\Gamma$ transitions) and i$^1\Pi$ state (i$^1\Pi$–a$^1\Delta$, $^1\Pi$–d$^1\Sigma^+$ transitions). The probability of approach along the singlet states is 2/189, except for the h$^1\Sigma^+$ state, which has a probability of 1/189. The variation of R_e with r for the f–a, f–c, f–b, c–a, b–a and b–d systems has been taken from Langhoff (1997) and that for i–a, i–d, b–h and c–g has been extracted from Dobrodey (2001).

The c–g system has the largest transition dipole moments among all the TiO transitions studied. However, the transition frequency is relatively small. Because of this, the contribution of this system to the total radiative association is very small. The f$^1\Delta$ and i$^1\Pi$ states are practically identical in energy, with the i$^1\Pi$ state slightly higher in energy, by only ~ 95 cm^{-1}. Since the transition moments of the f–a system are higher than those of i–a, the rate coefficients of the former transition are higher than those of the latter. The f–a, i–d, c–a and i–a transition frequencies, as the probability of approach along singlet states, are lower than those of the C–X transitions. Thus, the total rate coefficients through these transitions are smaller than those of the corresponding C–X (Figs 3 and 4). The transition frequencies

Table 2. Radiative association rate coefficients of TiO.

T (K)	k_{TiO} $(10^{-17}\,\mathrm{cm^3\,s^{-1}})$
300	4.76
700	6.11
1000	6.74
1500	7.46
2000	7.96
2500	8.33
3000	8.61
3500	8.84
4000	9.02
5000	9.28
6500	9.53
8500	9.73
10500	9.84
12500	9.92
14000	9.96

involved in the b–d, b–a and h–b systems are relatively small and these three molecule-forming transitions make little contribution to the total rate coefficients. Finally, the f–b and f–c transition dipole moments are relatively small, as well as the transition frequencies; these two transitions make a negligible contribution to the total rate coefficients compared with the C–X transition. The total rate coefficients for association through singlet–singlet transitions are found to vary from 1.66×10^{-17} to $3.24 \times 10^{-17}\,\mathrm{cm^3\,s^{-1}}$ for a temperature range 300–14 000 K, respectively.

For the $i^1\Pi$–$h^1\Sigma^+$, $i^1\Pi$–$b^1\Pi$, $h^1\Sigma^+$–$d^1\Sigma^+$ and $f^1\Delta$–$i^1\Pi$ systems, no information about dipole moments is available. However, the energy separation of these states and probability of approach along singlet states are lower than those for the C–X transition. Hence, the rate coefficients for radiative association through these channels are expected to be small.

Table 2 shows the total rate coefficients for radiative association of the TiO radical through singlet–singlet and triplet–triplet transitions. They are found to vary from 4.76×10^{-17} to $9.96 \times 10^{-17}\,\mathrm{cm^3\,s^{-1}}$ for temperatures ranging from 300–14 000 K, respectively, and can be approximated (within 3 per cent) as

$$k(T) = 5.94 \times 10^{-17} \left(\frac{T}{300}\right)^{0.1673} \exp\left(\frac{-65.099}{T}\right)\,\mathrm{cm^3\,s^{-1}} \quad (6)$$

for $300 \leq T \leq 5000$ K and

$$k(T) = 8.115 \times 10^{-17} \left(\frac{T}{300}\right)^{0.0557} \exp\left(\frac{-68.428}{T}\right)\,\mathrm{cm^3\,s^{-1}} \quad (7)$$

for $T > 5000$ K.

There are in addition four singlet and four triplet states that can be formed by the coupling of ground-state titanium and oxygen atoms. Among these, seven were established theoretically as $^3\Gamma$, $3^3\Delta$, $2^3\Phi$, $3^3\Pi$, $1^1\Sigma^-$, $2^1\Phi$ and $3^1\Pi$ (Miliordos & Mavridis 2010), which have estimated T_e values of 27 790, 29 704, 29 579, 29 456, 33 799, 29 761 and 30 226 cm^{-1}, respectively. There is also another singlet state, which is designated by $2^3\Sigma^+$. Among them, the systems $3^3\Delta$–$X^3\Delta$, $2^3\Phi$–$X^3\Delta$ and $3^3\Pi$–$X^3\Delta$ have large transition frequencies in relation to other systems and may be relevant for the formation of TiO by radiative association. However, the lack of transition dipole moments prevents us from considering the dipole-allowed transitions connecting these states.

12 quintet states can be formed from ground-state titanium and oxygen atoms: one Γ, two Φ, three Δ, three Π, two Σ^+ and one Σ^-. However, there appears to be no calculations of their properties.

For 1500 and 3000 K, our calculated radiative association rate coefficients for Ti and O atoms are 7.46×10^{-17} and $8.61 \times 10^{-17}\,\mathrm{cm^3\,s^{-1}}$, respectively. The corresponding rate coefficients for SiC are 1.89×10^{-17} and $1.93 \times 10^{-17}\,\mathrm{cm^3\,s^{-1}}$ (Andreazza, Vichietti & Marinho 2009) and those for SiS are 1.5×10^{-16} and $1.88 \times 10^{-16}\,\mathrm{cm^3\,s^{-1}}$ (Andreazza & Marinho 2007). These values show that Ti+O reactions tend to be more rapid than those of Si+C, but slower than those of Si+S. However, these values indicate that such reactions are much too slow to lead to significant TiO, SiC and SiS formation within the envelopes of stars.

4 CONCLUSIONS

We have calculated the rate coefficients for radiative association of Ti and O atoms to form the TiO molecule. The molecule-forming transitions occur dominantly through the $C^3\Delta$ state, followed by radiative transition to the $X^3\Delta$ state. Contribution to the total rate coefficients also comes from the A–X, f–a, c–a, b–a, i–a and i–d transitions of the TiO molecule.

The rate coefficients for the radiative association of TiO are of the order of 7.5×10^{-17}–$8.6 \times 10^{-17}\,\mathrm{cm^3\,s^{-1}}$ for temperatures of 1500–3000 K. These values indicate only a low efficiency for the radiative association reaction of Ti(^{3}F) and O(^{3}P) atoms and suggest that such a reaction is much too slow to lead to significant TiO formation in the extended photospheres of oxygen stars.

The main deficiency of the rate coefficients estimated for the formation of TiO by radiative association is the uncertainty related to quantum effects and the potential energy curves and their coupling elements at low temperatures. These effects should be considered in future work to ensure accurate rate coefficients at low temperatures. It is also desirable that transitions that have no dipole moment and have not been studied in this work are included in these studies, especially triplet–triplet transitions.

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APPENDIX A: THE POTENTIAL FUNCTION

The potential energy curves for the low-lying states of TiO were constructed using the empirical Hulbert–Hirschfelder function and are given by (Hulbert & Hirschfelder 1941, 1961)

$$U(r) = D_e \left[1 - e^{(-ax)^2} \right] + ca^3x^3e^{-2ax}(1 + bax), \qquad (A1)$$

where

$a = w_e/[2(B_eD_e)^{1/2}r_e] \, \mathrm{cm}^{-1}$,
$x = (r - r_e) \, \mathrm{cm}^{-1}$,
$c = 1 + a_1(D_e/a_0)^{1/2}$,
$b = 2 - [7/12 - (D_ea_2/a_0)]/c$,

with

$a_0 = w_e^2/4B_e$,
$a_1 = -1 - \alpha_e \, w_e/6B_e^2$,
$a_2 = 5a_1^2/4 - 2/3(w_ex_e/B_e)$.

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