## Semiclassical methods for calculating radiative association rate constants for different thermodynamic conditions: Application to formation of CO, CN, and SiN

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ARTICLE

### Semiclassical methods for calculating radiative association rate constants for different thermodynamic conditions: Application to formation of CO, CN, and SiN

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#### ABSTRACT

It is well-known that resonances can serve as a catalyst for molecule formation. Rate constants for resonance-induced molecule formation are phenomenological as they depend upon the mechanism used to populate the resonances. Standard treatments assume tunneling from the continuum is the only available population mechanism, which means long-lived quasibound states are essentially unpopulated. However, if a fast resonance population mechanism exists, the long-lived quasibound states may be populated and give rise to a substantial increase in the molecule formation rate constant. In the present work, we show that the semiclassical formula of Kramers and ter Haar [Bull. Astron. Inst. Neth. 10, 137 (1946)] may be used to compute rate constants for radiative association in the limit of local thermodynamic equilibrium. Comparisons are made with quantum mechanical and standard semiclassical treatments, and results are shown for two limits which provide upper and lower bounds for the six most important radiative association reactions leading to the formation of CO, CN, and SiN. These results may have implications for interstellar chemistry in molecular clouds, where the environmental and thermodynamic conditions often are uncertain.

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#### I. INTRODUCTION

The chemistry taking place in the interstellar medium has a great impact on the evolution of molecular clouds into new stars and planetary systems.<sup>1</sup> That is because during the gravitational contraction, the gas is heated due to the individual molecules' gain in kinetic energy as they "fall" toward the gravitational center of the interstellar cloud. Excess heat needs to be released to sustain the contraction into a new star. Through their rovibrational modes, molecules are efficient radiators at the wavelengths corresponding to the typical temperatures of a contracting molecular cloud. Thereby, molecules act as vital coolants in star forming processes as they transform gravitational energy into radiation energy.

Formation and destruction of molecules in the interstellar medium can happen in several ways. One mechanism of molecule formation is the radiative association reaction

$$A + B \to AB + \hbar\omega,$$
 (1)

where two colliding fragments A and B emit a photon during the encounter and thereby rid themselves of enough energy  $(\hbar\omega)$  to stabilize. Radiative association has very small rate constants for all molecular systems, and it can be ignored under atmospheric density conditions since other mechanisms of molecule formation that involves three body encounters will dominate. In the interstellar medium, however, the densities are often about  $10^{-15}$  times that of our atmosphere. It is an exotic environment and radiative



association plays a role, especially in regions where grains (dust particles) are rare.<sup>2</sup>

As the cross sections and rate constants are so small for radiative association, they are difficult to measure in a laboratory. Direct measurements have only been pursued with a handful of ionic species.<sup>3</sup> For neutral species and most ionic species, theoretical calculations need to be performed to provide astrochemists with data. Methods for calculation of radiative association rate constants have been developed over the past several decades. For the formation of diatomic molecules, see, e.g., the review by Nyman *et al.*<sup>4</sup> and references therein. Also, a few triatomic systems have been studied theoretically, e.g., Refs. 5–7. Whether the formed molecule is a diatom or a triatom, the computed cross sections are almost always full of sharp features, stemming from scattering resonances. These typically play a large role at low energies and thereby also in rate constants at low temperatures.

In the standard treatment of resonances, it is assumed that quasibound states may be populated through tunneling from the continuum. There are also Feshbach-type resonances where the system reaches a quasibound state through coupling between different electronic states. Studies of Feshbach resonances in radiative association have been performed, e.g., spin-orbit and rotational couplings,<sup>8</sup> but are rather limited. The main conclusions of the present work may be expected to hold also for Feshbach resonances, but none of our test systems involve them, so we will limit our discussion to shape resonances.

The role of shape resonances in molecule formation has recently been investigated for H<sub>2</sub>, SiO, and CS molecules.<sup>9-14</sup> It was shown that the choice of kinetic model can lead to mechanisms which compete with the standard treatment of populating the quasibound states and may result in a larger phenomenological rate constant. The upper limit of this increased rate constant is reached when the quasibound states are populated according to thermal equilibrium with the surrounding environment. This has been referred to as the local thermodynamic equilibrium (LTE) rate constant. The standard resonant treatment provides a lower limit, referred to as the non-LTE zero-density limit (NLTE-ZDL) rate constant, due to the absence of all population mechanisms (radiative as well as collisional) other than tunneling. In the LTE limit, the dominant population mechanism is likely to be three-body collisions. Therefore, it has been suggested<sup>13</sup> that the LTE rate constant for radiative association (RA) may be used to estimate three-body recombination (TBR) rates at the critical density<sup>15</sup> where collisional and radiative rates are the same. Since TBR rate constants are generally more challenging to compute than RA rate constants, it is desirable to calculate RA rate constants in both thermodynamic limits.

In this work, we revisit the role of resonances for the three molecules carbon monoxide (CO), cyano radical (CN), and silicon mononitride (SiN). The standard resonant treatment for these molecules has been reported previously.<sup>16–18</sup> Using the same molecular data, we carry out the present studies on the six reactions

$$C({}^{3}P) + O({}^{3}P) \to CO(A^{1}\Pi) \to CO(X^{1}\Sigma^{+}) + h\nu, \qquad (2)$$

$$C(^{3}P) + O(^{3}P) \to CO(2^{1}\Sigma^{+}) \to CO(X^{1}\Sigma^{+}) + h\nu, \qquad (3)$$

$$C({}^{3}P) + O({}^{3}P) \to CO(X^{1}\Sigma^{+}) \to CO(X^{1}\Sigma^{+}) + h\nu, \qquad (4)$$

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$$C(^{3}P) + N(^{4}S) \to CN(A^{2}\Pi) \to CN(X^{2}\Sigma^{+}) + h\nu, \qquad (5)$$

$$\operatorname{Si}({}^{3}P) + \operatorname{N}({}^{4}S) \to \operatorname{SiN}(A^{2}\Pi) \to \operatorname{SiN}(X^{2}\Sigma^{+}) + h\nu, \qquad (6)$$

$$\operatorname{Si}({}^{3}P) + \operatorname{N}({}^{4}S) \to \operatorname{SiN}(X^{2}\Sigma^{+}) \to \operatorname{SiN}(A^{2}\Pi) + h\nu, \qquad (7)$$

which are the most important reactions for RA of the three molecules.  $^{16\mathchar{-}18}$ 

#### **II. THEORY**

In the standard treatment of radiative association,<sup>5,19</sup> the formation process is divided into a direct and resonance mediated part as illustrated in Fig. 1. The direct process can often be well characterized with classical (CL) dynamics. For the case when the radiative association proceeds on one potential energy curve, as in Fig. 1, the direct radiative association can be computed with a method where both the atomic motion and the radiation are classical (CL).<sup>20</sup> If radiative association also involves a change in the electronic state, then the semiclassical (SC) method<sup>18,21</sup> is appropriate for diatomics, as well as semiclassical surface-hopping,<sup>22</sup> which appears to work also for the formation of polyatomics. Apart from molecule formation rate constants, those methods also allow for computation of emission spectra.<sup>22-24</sup> The standard semiclassical method for diatomic molecules may be modified so that it accounts for dynamics in the phase space behind the barrier by assuming the barrier is perfectly transparent. This simplified semiclassical (SC) method, which is described in Sec. II A, was first given by Kramers and ter Haar.<sup>25</sup> The simplified SC method is normally considered a poor approximation for systems which possess large barriers due to the assumption that quasibound states are populated only through tunneling. When this assumption is removed and fast mechanisms for populating the quasibound states are considered, the accuracy and utility of the simplified SC method should be reevaluated. As described below, we find that the simplified SC method performs surprisingly well when used in the appropriate thermodynamic limit.



**FIG. 1.** Schematic figure showing a potential energy curve and direct vs resonance mediated radiative association. The dotted green line is an energy level corresponding to a quasibound state, and the red solid line is for a true bound state. The barrier can be in the potential energy curve itself or a centrifugal barrier. The bound state may also be formed on a different potential energy curve.

The resonance mediated process is typically treated with the Breit-Wigner (BW) method, which will be outlined in Sec. II B. The BW rate constant may be derived by performing the thermal velocity integration analytically using a Lorentzian shape for the cross section. The Lorentzian width typically includes radiative broadening in order to ensure unitarity and avoid the so-called breakdown of perturbation theory which would otherwise occur for long-lived quasibound states.<sup>19</sup> If a competing kinetic mechanism is available, however, which is faster than the tunneling rate, then the population of quasibound states would increase and may give rise to a substantial increase in the rate constant.<sup>10</sup> If the competing mechanism is also faster than the radiative rate, then the population of quasibound states may reach the LTE limit.

The LTE and NLTE-ZDL rate constants represent limiting cases for the steady-state solution of a governing master equation which includes the various mechanisms that may be important for a given system. The master equation has been expressed in a square-integrable Sturmian basis set which includes transitions between all bound and unbound states, including long-lived quasibound states and discretized nonresonant states. This approach,<sup>9–11</sup> which is referred to as the Sturmian quantum kinetic theory (SQKT), is described in Sec. II C.

In previous work,<sup>12,13</sup> it was shown that the NLTE-ZDL rate constant computed by SQKT agrees well with the standard quantum rate constant computed using perturbation theory on a coarsely spaced energy grid and also with the semiclassical rate constant when the resonant contribution is small. In the present work, we find that the simplified SC rate constants agree very well with the LTE rate constants computed using the SC + BW and SQKT methods. The agreement improves when the potential energy curve of the entrance channel supports many quasibound states. Therefore, the simplified SC method adds another viable approach to the list of methods that are useful for computing RA rate constants under appropriate thermodynamic conditions. In Secs. II A–II C, we outline the different methods and provide numerical comparisons.

#### A. Standard and simplified SC rate constants

Semiclassical (SC) approaches for radiative association are appropriate when the radiation gives a change in the electronic state of the molecular system.<sup>4</sup> In the standard SC method for diatomics, 18,21,25 only the region of phase space at R outside the outer classical turning point is accounted for, i.e., the blue, continuum region in Fig. 1. In the simplified SC formula also, the region of phase space where quasibound states exist, i.e., the green dotted region in Fig. 1, is accounted for. Thus, it is expected to account for both direct and resonant radiative associations. The simplified SC formula was first derived by Kramers and ter Haar<sup>25</sup> and has later been rederived.<sup>21,26,27</sup> It has been tested for the essentially nonresonant radiative association reactions of HF in Ref. 23 and of H<sub>2</sub><sup>+</sup> in Ref. 28. In the work on H<sub>2</sub><sup>+</sup>, a correction of the simplified SC formula introduced by Bates<sup>21</sup> was investigated. The recommendation in Ref. 28 was that some care to include the Bates correction term should be exercised when applying the simplified SC formula to problems with significant barriers. We have not investigated Bates' correction in this work. Finally, a version of the simplified SC formula that is appropriate for dimer contributions in interaction-induced spectra has also been developed in recent years.<sup>29</sup>

The term *simplified* refers to that the evaluation of the rate constant is more straight forward than that of the standard formula. In the former, there is only a radial integral that has to be computed numerically, while in the latter, a three dimensional integral, over radial distance, R, kinetic energy, and impact parameter, has to be computed. The simplified SC rate constant for radiative association of a diatomic molecule at temperature T is

$$k_{C \to C'}(T) = 4\pi P_{\Lambda S} \int_0^\infty R^2 A_{C \to C'}(R) e^{-\beta V_C(R)} \\ \times [f_b(\beta V_{C'}(R)) - f_b(\beta V_C(R))] dR,$$
(8)

where

$$f_b(y) = \begin{cases} 0 & \text{if } y > 0\\ \frac{2}{\sqrt{\pi}} \int_0^{-y} \sqrt{x} e^{-x} dx & \text{otherwise} \end{cases}$$
(9)

is the incomplete gamma function.  $V_C(R)$  is the potential energy curve as a function of the interatomic distance, R, for molecular state C.  $\beta = 1/k_B T$ , where  $k_B$  is the Boltzmann constant. Unprimed and primed subscripts correspond to initial and final states, respectively, so that, for example, C and C' are  $2^1\Sigma^+$  and  $X^1\Sigma^+$ , respectively, for reaction (3). The term  $f_b(\beta V_{C'})$  in the brackets serves to include radiative transitions to bound states only, i.e., it excludes radiative quenching, while  $-f_b(\beta V_C)$  excludes transitions from bound states on the upper potential. The transition probability is defined as<sup>21,30</sup>

$$A_{C \to C'}(R) = \frac{4}{3c^3\hbar(4\pi\epsilon_0)} \left(\frac{2-\delta_{0,\Lambda+\Lambda'}}{2-\delta_{0,\Lambda}}\right) \omega_{C \to C'}^3(R) D_{CC'}^2(R), \quad (10)$$

where

$$\omega_{C \to C'}(R) = \frac{\max(0, V_C(R) - V_{C'}(R))}{\hbar}$$
(11)

is the frequency of the emitted radiation and  $D_{CC'}(R)$  is the transition dipole moment. c,  $\hbar$ , and  $\epsilon_0$  are the speed of light, the reduced Planck constant, and the permittivity of free space, respectively. The statistical weight factor for the approach in the diatomic state with orbital electronic angular momentum, projected on the molecular axis,  $\Lambda$ , and spin quantum number, S, is given by<sup>31</sup>

$$P_{\Lambda S} = \frac{(2S+1)(2-\delta_{0,\Lambda})}{(2L_A+1)(2S_A+1)(2L_B+1)(2S_B+1)},$$
(12)

where  $L_A$ ,  $S_A$ ,  $L_B$ , and  $S_B$  are the electronic orbital angular momentum and spin quantum numbers of atoms *A* and *B*, respectively. The statistical factors  $P_{\Lambda S}$  for the reactions we consider in this work are given in Refs. 16–18.

#### **B.** Resonant BW rate constants

Breit-Wigner (BW) theory<sup>32,33</sup> provides a method to compute a resonance mediated rate constant. The BW radiative association rate constant for the formation of diatomic molecules is given by<sup>5,19</sup>

$$k_{C \to C'}(T) = \frac{P_{\Lambda S}}{\hbar Q_T} \sum_{vj} (2j+1) \frac{e^{-\beta E_{vjC}}}{1/\Gamma_{vjC}^{\text{tun}} + 1/\Gamma_{vjC \to C'}^{\text{rad}}}.$$
 (13)

The quasibound states have vibrational and rotational quantum numbers v and j, and energy levels  $E_{vjC}$ . Each quasibound state has a width,  $\Gamma_{vjC}^{\text{tun}}$ , for tunneling to the continuum and a width  $\Gamma_{vjC\to C'}^{\text{rad}}$  for radiative decay to the final molecular state C'. The translational partition function is defined by  $Q_T = (2\pi\mu/\beta h^2)^{3/2}$ , where  $\mu$  is the reduced mass of the pair *AB*.

In Eq. (13), it is assumed that each quasibound state is populated and depopulated through tunneling only. If there is a competing mechanism  $\Gamma_{vjC}^{\text{fast}}$  that is much faster than the tunneling rate, then the BW formula (13) may be modified by the replacement  $\Gamma_{vjC}^{\text{tast}} \rightarrow \Gamma_{vjC}^{\text{fast}}$ . If the condition  $\Gamma_{vjC}^{\text{fast}} \gg \Gamma_{vjC \rightarrow C'}^{\text{rad}}$  also holds, then Eq. (13) yields the limiting rate constant

$$k_{C \to C'}(T) = \frac{P_{\Lambda S}}{\hbar Q_T} \sum_{vj} (2j+1) e^{-\beta E_{vjC}} \Gamma^{\text{rad}}_{vjC \to C'}$$
(14)

which is equivalent to the resonant part of the LTE formula described in Sec. II C if  $\Gamma_{vjC\to C'}^{rad}$  is computed by adding the partial widths for all transitions to *truly* bound states on C'. The rate constants (13) and (14) should provide good estimates for the lower and upper bounds of the phenomenological rate constant. In the SQKT described in Sec. II C, radiative transitions to lower-lying quasibound states are included in the calculation of the density of unbound states but not in the final sum over bound states.

#### C. SQKT rate constants

The Sturmian quantum kinetic theory (SQKT) described previously<sup>9-12</sup> uses square-integrable  $(L^2)$  basis sets to compute the rate constants. In this approach, the usual thermal velocity average is replaced by the density operator

$$\hat{\rho}_f = Q_T^{-1} \sum_f g_f \, e^{-\beta E_f} |f\rangle \langle f|,\tag{15}$$

where the discrete sum over "free" states is obtained by diagonalizing the noninteracting Hamiltonian in the  $L^2$ -basis. Here,  $E_f$  is the energy eigenvalue and  $g_f = (2j_f + 1)$  is the degeneracy of the free state  $f = \{v_f, j_f\}$  represented by vibrational and rotational quantum numbers. The length scale and number of Sturmian basis functions should be sufficient<sup>9</sup> to ensure  $\text{Tr}(\hat{p}_f) = 1$ . The density operator for the unbound states of the interacting system may be written as

$$\hat{\rho}_u = Q_T^{-1} \sum_u c_u g_u e^{-\beta E_u} |u\rangle \langle u|, \qquad (16)$$

where  $u = \{v_u, j_u\}$  represents a positive energy  $L^2$  eigenstate of an entrance Hamiltonian in Eqs. (2)–(7) with degeneracy  $g_u = g_f P_{\Lambda S}$ . The relative population coefficient  $c_u$  may be computed from the steady-state solution of a Sturmian master equation that includes all relevant kinetic pathways. The expression of the RA rate constant obtained using the density operator (16) takes the form

$$k_{C \to C'}(T) = \frac{P_{\Lambda S}}{\hbar Q_T} \sum_{b,u} c_u \left(2j_u + 1\right) e^{-\beta E_u} \Gamma_{u \to b}^{rad},\tag{17}$$

where  $\Gamma_{u\to b}^{rad}$  is the matrix element for spontaneous emission to a bound state  $b = \{v_b, j_b\}$  of the exit channel. For a closed system at constant *T*, it is easy to show that  $c_u = 1$  for all states. This has been referred to in Refs. 9–14 as the LTE limit. When the system

exchanges energy with its surroundings, such as the exiting photons produced by RA, the population of resonant unbound states may be nonthermal, and the master equation should be used to compute the NLTE coefficients. If there are no excitation mechanisms available to the system, the steady-state solution of the master equation yields

$$c_u = \frac{\Gamma_u^{tun}}{\Gamma_u^{tun} + \Gamma_u^{rad}},\tag{18}$$

where  $\Gamma_u^{rad}$  is computed by summing over all possible decay channels. This was referred to in Refs. 13 and 14 as the NLTE-ZDL solution. The NLTE-ZDL and LTE rate constants appear very similar to the BW formulas (13) and (14). We note, however, that the sum over unbound states in Eq. (17) includes both resonant and nonresonant states, so there is no need to supplement this formula with a semiclassical or classical calculation of the direct contribution. It is also worth noting that  $\Gamma_u^{rad}$  includes transitions to lower-energy unbound states, whereas  $\Gamma_{u \to b}^{rad}$  in the rate formula (17) only includes transitions to bound states.

#### **III. RESULTS**

We have computed radiative association rate constants for the formation of three different diatomic molecules CO, CN, and SiN through the six reactions (2)-(7). Reactions (2)-(4) are treated using the same potential and dipole data as in Ref. 16, reaction (5) with the *ab initio* potential and dipole data from Ref. 8, and reactions (6) and (7) with the same data as in Ref. 18. The direct contributions are computed with semiclassical (SC) and classical (CL) formulas as described, for example, in Refs. 18 and 20, respectively. The numerical implementation of the simplified SC formula, which is described in Sec. II A, is done as described in Ref. 23. The resonance parameters needed for the BW formulas are computed with LEVEL<sup>34</sup> The LTE and NLTE-ZDL rate constants are computed using the SQKT formulation described in Sec. II C.

Figure 2 shows the rate constant for radiative association of CO through reaction (2). This reaction has a barrier, so the conventional



FIG. 2. Radiative association rate constants for the formation of CO through reaction (2). The rate constants were computed using the simplified SC, SC + BW, and SQKT methods in the two thermodynamic limits LTE and NLTE-ZDL.

treatment of resonances results in a rather small rate constant at low temperatures, which grows fast with increasing temperature. The LTE limit yields a larger rate constant, which is weakly decreasing with increasing temperature. From a few hundred Kelvins and up, there is good agreement between the simplified SC curve and the SC + BW and SQKT curves in the LTE limit. At the lowest temperatures, the simplified SC rate constant departs from the other two curves due to details of the resonances which are accounted for in the quantum treatments. Good agreement is also seen between the two NLTE-ZDL curves, especially at the higher temperatures. There is a difference at the lowest temperatures, which is evidently due to uncertainties in the SQKT calculation of the tunneling widths for the low energy resonances of this reaction that are supported by a shallow long-range well that lies outside of the barrier.

Figure 3 shows CO production through reaction (3). Also in this case, there is perfect agreement between the simplified SC treatment and LTE at a few hundred Kelvins and above. For this reaction, it is particularly difficult to obtain parameters for the most narrow resonances using a grid-based method such as LEVEL. This is due to features of the  $2^{1}\Sigma^{+}$  potential that are described in Ref. 16. For this reason, we have not been able to obtain a reliable SC + BW result for this reaction in the LTE limit. For NLTE-ZDL, the SC + BW rate constant is underestimated at the lowest temperatures for the same reason. The SQKT and SC + BW results agree reasonably well from a few hundred Kelvins and above. Note that for this reaction, the influence of the resonances is very small above 2000 K, independent of which kinetic model is used. Thus, all four curves coincide above roughly 3000 K.

In the supplementary material, we repeat the LTE calculations shown in Figs. 2 and 3 for the <sup>13</sup>C isotope. The increased mass has no effect on the simplified SC result; however, it compresses and shifts the eigenvalues of the quantum calculations toward lower energies. For the  $A^1\Pi \rightarrow X^1\Sigma^+$  transition, there are a large number of bound and quasibound states in the entrance channel, so the shifted spectrum brings the LTE rate constant into better agreement with the simplified SC curve. For the  $2^1\Sigma^+ \rightarrow X^1\Sigma^+$  transition, there are a small number of quasibound states in the entrance channel. The



FIG. 3. As in Fig. 2 but for reaction (3). The LTE result using the SC + BW formula is not included for this reaction (see explanation in the text).



FIG. 4. Radiative association rate constants for the formation of CO through reaction (4). In this case, the direct contribution in the results shown with dashed lines is computed with the classical (CL) formula as explained in Ref. 20.

increased reduced mass shifts the lowest energy quasibound state for  $^{12}$ CO into a bound state for  $^{13}$ CO. Consequently, the LTE rate constant for  $^{13}$ CO drops well below the simplified SC value at low temperature.

Reaction (4) takes place in absence of electronic transitions due to the permanent dipole moment of CO. This has two main consequences. First, the rate constants are typically 3–4 orders of magnitude smaller than for reactions where electronic transitions take place.<sup>17</sup> Second, the semiclassical formulation is not applicable. Figure 4 shows the corresponding computed rate constants with the remaining methods. The agreement between CL + BW and SQKT is essentially perfect for both LTE and NLTE-ZDL over the whole temperature interval (10 K–10 000 K). This reaction is barrier free, which results in a weakly increasing NLTE-ZDL rate constant vs temperature and a decreasing LTE rate constant. From 1000 K and up, the rate constants decrease rapidly as radiative quenching is favored at the cost of radiative association. This phenomenon has been seen previously, e.g., in radiative association of SiO<sup>12</sup> and HF.<sup>22</sup>





FIG. 6. As in Fig. 2 but for the formation of SiN through reaction (6).

In Fig. 5, the rate constants for CN formation through reaction (5) are displayed. This reaction is barrier free, and the behavior of the rate constants is qualitatively similar to that of reaction (4); however, the rate constants for reaction (5) are at least three orders of magnitude larger due to the (Franck-Condon type) integral in the dipole matrix element, which is larger when there is a change in the electronic state.<sup>4</sup> Again, the agreement of the simplified SC, SC + BW, and SQKT treatments is nearly perfect for LTE, apart from some small deviation below 20 K. For NLTE-ZDL, the SQKT and SC + BW results are in excellent agreement over the whole temperature interval.

For radiative association through transitions between two electronic molecular states, it is well known that transitions from an upper to a lower potential energy are preferred, rather than from a lower to an upper.<sup>21</sup> For SiN, the potential curves of the two molecular states that are involved in reactions (6) and (7) cross at an atomic separation of about 3.3 bohrs; outside that distance, the  $X^2\Sigma^+$  state has a larger potential energy than the  $A^2\Pi$  state. Since this crossing is located in the strong interaction region, both reactions (6) and (7) contribute significantly to the total SiN rate constant. In Figs. 6 and 7, the rate constants are displayed, and again, we see



agreement between the different methodologies in the two thermodynamic limits. Because the  $A^2\Pi$  potential supports more low energy quasibound states than the  $X^2\Sigma^+$  potential, the agreement between the simplified SC rate constant and the LTE result is better at low temperatures for reaction (6) than for reaction (7).

#### **IV. CONCLUSION**

In the present work, we have compared several methods for computation of RA rate constants. Because environmental conditions can influence the resonance contribution to molecule formation, we have computed RA rate constants for two limits which provide upper and lower bounds for the formation of three diatomic molecules, CO, CN, and SiN. The dominant transitions have been considered in each case. We have verified numerically that the simplified SC method provides an excellent approximation in the LTE limit when the potential energy curve of the entrance channel supports a large number of quasibound states. For the molecular systems considered in the present work, the simplified SC method yields near-perfect agreement with the quantum calculations above a temperature of about 100 K.

The good agreement between the simplified SC and LTE rate constants found in the present work mirrors the agreement found previously<sup>13</sup> for the standard SC and NLTE-ZDL rate constants computed by SQKT and perturbation theory with a coarsely-spaced energy grid (the grid resolved broad resonances but not narrow ones in order to achieve the agreement). It is also shown here that the standard SC result may be used together with the usual BW formula in the appropriate limit to get both the NLTE-ZDL and LTE rate constants. Calculating the total rate constant by adding the resonance contribution, computed with the BW formula using the appropriate mechanism, to a semiclassical or classical result, therefore, is essentially equivalent to the SQKT result in both thermodynamic limits, apart from the minor differences in accounting for downward transitions to quasibound states.

In an interstellar environment where a fast mechanism other than tunneling from the continuum contributes to the population of quasibound states, the same fast mechanism would also contribute to the population of true bound states and perhaps be the dominant mechanism for molecule formation. The LTE result, therefore, provides a useful estimate of the crossover from RA to the dominant molecule formation mechanism (e.g., TBR). If the critical density for the crossover is known, then the TBR rate coefficient may be obtained from the RA rate constant and used at higher densities where RA is unimportant.<sup>13</sup> Therefore, it is useful to compute RA rate constants in both thermodynamic limits. Standard quantum rate constants for the present systems have been reported previously.<sup>16-18</sup> These rate constants are appropriate for very low gas densities and weak radiation fields where the NLTE-ZDL assumption applies. In the supplementary material, we provide new data for the present systems that may be used in the LTE limit. Further studies of environmental influences on competing types of chemical reactions would also be desirable.

#### SUPPLEMENTARY MATERIAL

Figure 1 of the supplementary material shows the LTE rate constant for reactions (2) and (3) for the formation of the different isotopes <sup>12</sup>CO and <sup>13</sup>CO. It illustrates that if there is a high density of quasibound states, which is the case for reaction (2), then the rate constant is not sensitive to isotopes' effects. In reaction (3), only a few quasibound states contribute to the low temperature rate constant and a small shift of the quasibound energy levels, which is due to the small change in reduced mass, has a big effect. The rate constant computed with the simplified SC method is isotope independent since Eq. (8) does not contain the reduced mass. All calculations involving carbon in this work, other than that presented in Fig. 1 of the supplementary material, are for <sup>12</sup>C even though it is not explicitly stated. Tables I–VI of the supplementary material contain LTE rate constants for all six reactions (2)–(7).

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#### REFERENCES

- <sup>1</sup>E. Herbst, Chem. Soc. Rev. 30, 168-176 (2001).
- <sup>2</sup>J. F. Babb and K. P. Kirby, "Molecule formation in dust-poor environments," in *The Molecular Astrophysics of Stars and Galaxies*, edited by T. W. Hartquist and D. A. Williams (Clarendon Press, Oxford, 1998) p. 11.
- <sup>3</sup>D. Gerlich and S. Horning, Chem. Rev. **92**, 1509 (1992).

<sup>4</sup>G. Nyman, M. Gustafsson, and S. V. Antipov, Int. Rev. Phys. Chem. **34**, 385–428 (2015).

<sup>5</sup>F. Mrugała, V. Špirko, and W. P. Kraemer, J. Chem. Phys. **118**, 10547–10560 (2003).

<sup>6</sup>M. Ayouz, R. Lopes, M. Raoult, O. Dulieu, and V. Kokoouline, Phys. Rev. A 83, 052712 (2011).

<sup>7</sup>T. Stoecklin, P. Halvick, H.-G. Yu, G. Nyman, and Y. Ellinger, Mon. Not. R. Astron. Soc. **475**, 2545–2552 (2018).

<sup>8</sup>S. V. Antipov, M. Gustafsson, and G. Nyman, J. Chem. Phys. 135, 184302 (2011).
<sup>9</sup>R. C. Forrey, Phys. Rev. A 88, 052709 (2013).

<sup>10</sup>R. C. Forrey, J. Chem. Phys. **143**, 024101 (2015).

- <sup>11</sup>R. C. Forrey, J. Phys. B: At., Mol. Opt. Phys. 49, 194002 (2016).
- <sup>12</sup>R. C. Forrey, J. F. Babb, P. C. Stancil, and B. M. McLaughlin, J. Phys. B: At., Mol. Opt. Phys. **49**, 184002 (2016).
- <sup>13</sup> M. Cairnie, R. C. Forrey, J. F. Babb, P. C. Stancil, and B. M. McLaughlin, Mon. Not. R. Astron. Soc. 471, 2481 (2017).

<sup>14</sup>R. C. Forrey, J. F. Babb, P. C. Stancil, and B. M. McLaughlin, Mon. Not. R. Astron. Soc. 479, 4727–4734 (2018).

<sup>15</sup>Preliminary tests suggest that it may be sufficient to use the critical density for low-lying rovibrational levels to obtain such estimates.

<sup>16</sup>M. Gustafsson and G. Nyman, Mon. Not. R. Astron. Soc. 448, 2562–2565 (2015).

<sup>17</sup>S. V. Antipov, T. Sjölander, G. Nyman, and M. Gustafsson, J. Chem. Phys. 131, 074302 (2009).

<sup>18</sup>M. Gustafsson, S. V. Antipov, J. Franz, and G. Nyman, J. Chem. Phys. 137, 104301 (2012).

<sup>19</sup>O. J. Bennett, A. S. Dickinson, T. Leininger, and F. X. Gadéa, Mon. Not. R. Astron. Soc. **341**, 361–368 (2003); Erratum, **384** 1743 (2008).

<sup>20</sup> M. Gustafsson, J. Chem. Phys. **138**, 074308 (2013).

<sup>21</sup>D. R. Bates, Mon. Not. R. Astron. Soc. 111, 303 (1951).

<sup>22</sup> P. Szabó and M. Gustafsson, J. Chem. Phys. 147, 094308 (2017).

<sup>23</sup> M. Gustafsson, M. Monge-Palacios, and G. Nyman, J. Chem. Phys. 140, 184301 (2014).

<sup>24</sup>A. Tajti, G. Lendvay, and P. G. Szalay, "Dimol emission of oxygen made possible by repulsive interaction," J. Phys. Chem. Lett. 8, 3356–3361 (2017).

<sup>25</sup>H. A. Kramers and D. ter Haar, Bull. Astron. Inst. Neth. **10**, 137–146 (1946).

<sup>26</sup>P. S. Julienne, J. Chem. Phys. 68, 32–41 (1978).

<sup>27</sup>A. S. Dickinson, private communication (2010).

<sup>28</sup>D. E. Ramaker and J. M. Peek, "Molecule formation in tenuous media: Quantum effects in spontaneous radiative association," Phys. Rev. A **13**, 58–64 (1976).

<sup>29</sup>Y. N. Kalugina, S. E. Lokshtanov, V. N. Cherepanov, and A. A. Vigasin, J. Chem. Phys. **144**, 054304 (2016).

<sup>30</sup>B. Zygelman and A. Dalgarno, Phys. Rev. A 38, 1877–1884 (1988).

<sup>31</sup>C. M. Andreazza, P. D. Singh, and G. C. Sanzovo, Astrophys. J. **451**, 889 (1995); Erratum, **475**, 853 (1997).

<sup>32</sup>G. Breit and E. Wigner, Phys. Rev. **49**, 519 (1936).

<sup>33</sup>R. A. Bain and J. N. Bardsley, J. Phys. B 5, 277 (1972).

<sup>34</sup>R. J. Le Roy, University of Waterloo Chemical Physics Research Report No. CP-663, 2007.