Dicarbon formation in collisions of two carbon atoms

Babb, J., Smyth, R., & McLaughlin, B. (2019). Dicarbon formation in collisions of two carbon atoms. *The Astrophysical Journal, 876*(1). https://doi.org/10.3847/1538-4357/ab1088

**Published in:**
The Astrophysical Journal

**Document Version:**
Publisher's PDF, also known as Version of record

**Queen's University Belfast - Research Portal:**
Link to publication record in Queen's University Belfast Research Portal

**Publisher rights**
Copyright 2019 the authors. This is an open access article published under a Creative Commons Attribution License (https://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution and reproduction in any medium, provided the author and source are cited.

**General rights**
Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

**Take down policy**
The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.
Dicarbon Formation in Collisions of Two Carbon Atoms

James F. Babb1 ⊗, R. T. Smyth1,2 ⊗, and B. M. McLaughlin1,2 ⊗

1 Institute for Theoretical Atomic, Molecular, and Optical Physics, Center for Astrophysics | Harvard & Smithsonian, 60 Garden Street, Cambridge, MA 02138, USA
jbabb@cfa.harvard.edu, rsmyth41@qub.ac.uk, bmlaughlin899@btinternet.com
2 Centre for Theoretical Atomic, Molecular, and Optical Physics, School of Mathematics & Physics Queen’s University of Belfast, Belfast BT7 1NN, Northern Ireland, UK

Received 2019 February 11; revised 2019 March 8; accepted 2019 March 14; published 2019 April 30

Abstract

Radiative association cross sections and rates are computed, using a quantum approach, for the formation of C2 molecules (dicarbon) during the collision of two ground-state C(2P) atoms. We find that transitions originating in the C 1Πu, 3Πg, and 1 3Πu states are the main contributors to the process. The results are compared and contrasted with previous results obtained from a semiclassical approximation. New ab initio potential curves and transition dipole moment functions have been obtained for the present work using the multi-reference configuration interaction approach with the Davidson correction (MRCI+Q) and aug-cc-pCV5Z basis sets, substantially increasing the available molecular data on dicarbon. Applications of the current computations to various astrophysical environments and laboratory studies are briefly discussed, focusing on these rates.

Key words: ISM: supernova remnants – molecular data – molecular processes

1. Introduction

Dicarbon (C2) was first observed spectroscopically in flames and arcs and continues to be a useful diagnostic there and in carbon plasmas for other laboratory and industrial applications (Nemes & Irle 2011). The molecule has been observed in a host of extraterrestrial sources such as comets, carbon stars, protoplanetary nebulae, and molecular clouds. Interstellar dicarbon has been detected at optical wavelengths in diffuse (Chaffee & Lutz 1978; van Dishoeck et al. 1993; Gredel et al. 2001) and translucent (van Dishoeck & Black 1989; Iglesias-Groth 2011) molecular clouds. The optical detection of C2 in comets is an element of their classification into “typical” and “depleted” (A’Hearn et al. 1995; Cochran et al. 2012). Dicarbon is present in solar (Lambert 1978) and model stellar atmospheres, including the pioneering work of Tsuji (1964) and Lord (1965), and seen, for example, in solar optical (Grevesse & Sauval 1973) and infrared spectra (Brault et al. 1982), and in infrared spectra of carbon-rich giant stars (Goebel et al. 1983; Lodid 2001). The presence of the Swan bands of dicarbon (optical wavelengths) is an important element in the classification scheme of carbon stars (Keenan 1993; Green 2013). The mechanisms of formation of dicarbon vary, depending on the operative chemistries. For example, in diffuse molecular clouds dissociative recombination of CH2+ leads to C2 (Black & Dalgarno 1977; Federman & Huntress 1989), while in comets a chemistry starting with photodissociation of C2H2 or C3H may be operative (Jackson 1976).

Of particular interest for the present work is the formation of carbonaceous dust in the ejecta of core-collapse supernovae, where the formation of dicarbon through radiative association (R.A.) enters chemical models (Liu et al. 1992; Cherchneff & Dwek 2009; Clayton & Meyer 2018; Sluder et al. 2018) and is an initial step in models of formation of larger carbon clusters through condensation (Clayton et al. 1999, 2001; Clayton 2013) or nucleation (Lazzati & Heger 2016). (Later, in Section 4, we discuss in more detail laboratory experiments on carbon vapors generated by laser radiation. We note at this point that evidence of associative collisions of two ground-state carbon atoms was found by Monchicourt (1991) in light emission from laser-induced expansion of carbon vapor from a graphite rod.) Figure 1 illustrates a sample of the experimentally observed bands (Tanabashi et al. 2007; Bornhauser et al. 2015; Furtenbacher et al. 2016; Macrae 2016) connecting 1 singlet, triplet, and quintet states of the C2 molecule that contribute to the overall R.A. rate coefficient for this molecule. In the ejecta of SN 1987A and other core-collapse supernovae, CO and SiO were detected (Checherneff & Sarangi 2011; Sarangi et al. 2018), through fundamental (Δν = 1) bands3 of ground molecular electronic states allowing observational tests of molecular formation models (Liu et al. 1992; Liu & Dalgarno 1995; Cherchneff & Sarangi 2011; Sarangi & Cherchneff 2013; Rho et al. 2018)—dicarbon, however, lacks a permanent electric dipole moment and analogous vibrational transitions (fundamental bands) do not exist, making reliable theoretical predictions of rate coefficients imperative. Moreover, recent three-dimensional mapping of CO and SiO in the SN 1987A core ejecta with the Atacama Large Millimeter/submillimeter Array (ALMA) shows a clumpy mixed structure calling for improvements beyond one-dimension in hydrodynamical and chemical modeling of molecular formation (Abellán et al. 2017); a reliable description of dicarbide formation might improve such future calculations. Finally, understanding the origins of cosmic dust and the roles played by supernovae in contributing to extragalactic dust depends on progress in modeling dust formation (Sarangi et al. 2018; Sluder et al. 2018).

The R.A. rate was originally estimated to have a rate coefficient kR.A. ≈ 1 × 10⁻¹⁷ cm³ s⁻¹ (Prasad & Huntress 1980; Millar et al. 1991) for theoretical models of interstellar clouds;

---

3 CO was also detected in the first overtone band (Δν = 2). In SN 1987A, individual rotational lines of CO and of SiO were detected at late epoch; see Abellán et al. (2017) and Sarangi et al. (2018).
subsequent semiclassical calculations (Andreazza & Singh 1997) found comparable values with a weak temperature dependence increasing from $3.07 \times 10^{-18}$ cm$^{-1}$ s$^{-1}$ at 300 K to 1.65 $\times 10^{-17}$ cm$^{-1}$ s$^{-1}$ at 14,700 K. In recent studies using a quantum approach on systems such as SiP (Golubev et al. 2013), SiO (Forrey et al. 2016; Cairnie et al. 2017), and CS (Forrey et al. 2018; Pattillo et al. 2018) it was found that the semiclassical calculations (Andreazza & Singh 1997; Andreazza et al. 2006) underestimated the cross sections and rates, particularly at low temperatures.

In the present study we obtain results from a quantum approach to estimate the cross sections and rate coefficients for C$_2$ formation by R.A. using new highly accurate ab initio molecular data for the potential energy curves (PECs) and transition dipole moments (TDMs) coupling the states of interest. Results from our present quantum approach are compared with the previous semiclassical results of Andreazza & Singh (1997) and conclusions are drawn.

This paper is organized as follows. An overview of how the molecular data is obtained for our dynamical calculations is presented in Section 2. In Section 3, a brief overview of the R.A. cross section and rates are outlined. The computed R.A. cross sections and rates are presented in Section 3 and are compared with the previous semiclassical work of Andreazza & Singh (1997) in Section 4. Finally, Section 5 provides conclusions. Atomic units are used throughout unless otherwise specified.

2. Theory and Calculations

2.1. Potential Curves and TDMs

In a similar manner to our recent all-electron molecular structure and the resulting dynamical studies on diatomic systems such as SiO (Forrey et al. 2016; Cairnie et al. 2017), CS (Forrey et al. 2018; Pattillo et al. 2018), HeC$^+$ (Babb & McLaughlin 2017a), SH$^+$ (Shen et al. 2015; McMullan et al. 2016), CH$^+$ (Babb & McLaughlin 2017b), and HeAr$^+$ (Babb & McLaughlin 2018), the PECs and TDMs for the 18 singlet, triplet, and quintet electronic states are calculated within an MRCI+Q approximation for the approach of ground-state carbon atoms. That is, we use a state-averaged-multi-configuration-self-consistent-field (SA-MCSCF) approach, followed by multi-reference configuration interaction (MRCI) calculations together with the Davidson correction (MRCI+Q) (Helgaker et al. 2000). The SA-MCSCF method is used as the reference wave function for the MRCI calculations. Lying singlet, triplet, and quintet electronic states and the transition dipole matrix elements connecting these molecular states are calculated and used in the present dynamical calculations for the R.A. process. The literature on the molecular properties of dicarbon is extensive; sources with comprehensive bibliographies include Martin (1992), Nemes & Irle (2011), Zhang et al. (2011), Boschen et al. (2014), Macrae (2016), Furtenbacher et al. (2016), Yurchenko et al. (2018), and Varandas & Rocha (2018).

PECs and TDMs as a function of internuclear distance, $R$, are calculated starting from a bond separation of $R = 1.5$ Bohr extending out to $R = 20$ Bohr. The basis sets used in the present work are the augmented correlation consistent polarized core valence quintuplet (aug-cc-pVQZ (AVQZ)) Gaussian basis sets. The use of such large basis sets is well known to recover 98% of the electron correlation effects in molecular structure calculations (Helgaker et al. 2000). All of the PEC and TDM calculations for the C$_2$ molecule were performed with the quantum chemistry program package MOLPRO 2015.1 (Werner et al. 2015), running on parallel architectures.

For molecules with degenerate symmetry, an Abelian subgroup is required to be used in MOLPRO. Therefore, for a diatomic molecule like C$_2$ with D$_{\text{ac}}$ symmetry, it will be substituted by D$_{3h}$ symmetry with the order of irreducible representations being $(A_g, B_3g, B_1g, B_1u, B_2u, B_3u, A_u)$. When symmetry is reduced from D$_{\text{ac}}$ to D$_{3h}$, (Herzberg 1950), the correlating relationships are $\sigma_g \rightarrow a_u$, $\sigma_u \rightarrow a_u$, $\pi_g \rightarrow (b_{2g}, b_{3g})$, $\pi_u \rightarrow (b_{2u}, b_{3u})$, $\delta_g \rightarrow (a_g, b_{1g})$, and $\delta_u \rightarrow (a_u, b_{1u})$.

To account for short-range interactions, we employed the nonrelativistic, state-averaged complete active-space-self-consistent-field (SA-CASSCF)/MRCI method available within the MOLPRO (Werner et al. 2012, 2015) quantum chemistry suite of codes.

For the C$_2$ molecule, molecular orbitals (MOs) are put into the active space, including $(3a_u, 1b_{3u}, 1b_{2u}, 0b_{1g}, 3b_{1u}, 1b_{2g}, 1b_{3g}, 0a_u)$, symmetry MOs. The MOs for the MRCI procedure were obtained using the SA-MCSF method; for singlet and triplet spin symmetries, we carried out the averaging processes on the two lowest states of the symmetries $(A_g, B_3u, B_1g, B_1u)$ and the lowest states of the symmetries $(B_3u, B_3g, B_2g$ and $A_u$). A similar approach was also used for the quintet states. This approach provides an accurate representation of the singlet, triplet, and quintet states of interest as the molecule dissociated.

At bond separations beyond $R = 14$ Bohr, the PECs are smoothly fitted to functions of the form

$$V(R) = \frac{C_5}{R^5} - \frac{C_6}{R^6},$$  

where for the particular electronic state, $C_5$ is the quadrupole–quadrupole electrostatic interaction (Knipp 1938; Chang 1967), and $C_6$ is the dipole–dipole coefficient (Knipp 1938 and by Boggio-Pasqua et al. (2000) (for singlet and triplet $\Sigma$, $\Pi$ and $\Delta$ electronic states, which suffices to determine those for quintet states by symmetry). The long-range dispersion coefficient $C_6$ (averaged over the possible fine structure levels of two carbon atoms) was calculated to be $40.9 \pm 4.4$ using the many-body...
perturbation theory by Miller & Kelly (1972), and estimated to be 46.29 using the London formula by Chang (1967). In fitting the long-range form Equation (1) to the calculated potential energy data, we adjusted the values of $C_5$ and $C_6$ as necessary to match the slopes of the PECs. The adopted values are given in Table 1. We began with estimates of $C_5$ from Knipp (1938) and Boggio-Pasqua et al. (2000) and limited our adjustment of $C_6$ to either the value of Miller & Kelly (1972) or that of Chang (1967). For the $B^1\Sigma^+_g$ state, there is a barrier in the PEC (0.0086 eV or 69 cm$^{-1}$ at $R = 7.12$), reflected in the positive value of $C_5$ which fit the data. This is in good accord with a value found by Varandas (2008), 43 cm$^{-1}$ at $R = 8.37$, in an extensive study of diabatic representations of the $X^1\Sigma^+_g$ and $B^1\Sigma^+_g$ states. (This barrier energy is too low to appreciably affect the dynamics calculations presented below.)

As a consequence of fitting the potentials to Equation (1), the calculated potentials (as output from MOLPRO) were shifted. In Table 1 we list the final values of $T_e$ (in cm$^{-1}$) relative to the minimum of the $X^1\Sigma^+_g$ PEC, and the term energies are plotted schematically in Figure 1 for experimentally observed bands. Our calculated values may be compared with the recent experimental fits in Table 4, column 3, of Furtenbacher et al. (2016), and we agree to within 100 cm$^{-1}$ for the $a^3\Pi_m$, $A^1\Pi_n$, $c^3\Sigma^+_u$, and $B^1\Delta_n$ states, and to within 205 cm$^{-1}$ for the $b^3\Sigma^+_g$ and $B^3\Sigma^+_g$ states. (Expressed with respect to the minimum of the $a^3\Pi_n$ curve and calculated using the aug-cc-pV5Z basis sets). Our calculated $1^1\Pi_n$ state supports a shallow that is well in agreement with previous calculations (Bruna & Grein 2001; Bornhauser et al. 2015; Visser et al. 2019), deepening the shelf-like form of the curve found in the earlier calculations of Kirby & Liu (1979). The accuracy of the present PECs is very satisfactory for the purposes of the present study. The potential curves for $C_5$ singlet, triplet, and quintet states are shown in Figure 2. Structures due to nonadiabatic couplings are apparent in the $c^3\Sigma^+_u$ and $2^3\Sigma^+_u$ curves, due to their mutual interaction and interactions with higher states (see Figure 3 of Kirby & Liu 1979). As we will show below, the calculated cross sections involving the $c^3\Sigma^+_u$ and $2^3\Sigma^+_u$ states are several orders of magnitude smaller than those from the leading transitions contributing to the total R.A. cross sections. Similar structures in the quintet states (Bruna & Grein 2001) occur at energies at about 1 eV corresponding to kinetic temperatures above the range of the present study. Thus, we ignore nonadiabatic couplings and expect that they will have at most a minor effect on the net total cross sections for R.A.

The TDMs for the $C_2$ molecule are similarly extended to long- and short-range intermolecular distances. For $R > 14$, a functional fit of the form $D(R) = a \exp(-bR) + c$ is applied, while in the short-range $R < 1.5$ a quadratic fit of the form $D(R) = aR^2 + bR + c$ is adopted.

The TDMs for singlet transitions are shown in Figure 3, for triplet transitions in Figure 4, and for quintet transitions in Figure 5. As shown in Figures 3 and 4, the results are in satisfactory agreement with previous calculations for the Phillips, Swan, Ballik-Ramsay, and Schmidt-Kable (Duck) bands (ONeil et al. 1987; Langhoff et al. 1990; Kokkin et al. 2007; Brooke et al. 2013). In addition, our results for the Bernath $B^1\Sigma^+_g$–$A^1\Pi_n$ and Deslandres-d’Azambuja bands are provided over a substantially larger range of intermolecular distances compared with the earlier MRDCI calculations of Chabalowski et al. (1983). The band $1^3\Sigma^+_u$–$1^1\Pi_n$ has not yet been observed (Bornhauser et al. 2015); we point out that $2^3\Sigma^+_u$–$d^3\Pi_n$, $1^3\Delta_n$–$d^3\Pi_n$, and $1^3\Delta_n$–$1^3\Pi_n$ bands may exist. Additionally, we observe that the $2^3\Sigma^+$–$d^3\Pi_n$ band might contribute at wave numbers where significant spectral congestion is seen in dicarbon (Tanabashi et al. 2007).

### 3. Cross Sections

The quantum mechanical cross section for the R.A. process $\sigma_{\text{QM}}(E)$, where the initial, $i$, and final, $f$, electronic states are labeled by their molecular states (e.g., $d^3\Pi_n$), can be calculated using perturbation theory (see, for example, Babb & Dalgarno 1995; G mastering & Gori Giorgi 1996 and Babb & Kirby 1998). The result is

$$
\sigma_{\text{QM}}(E) = \sum_{i<j} \sum_{I,J} \frac{64}{3} \frac{\pi^4}{137.0369} \frac{\nu^3}{2\mu E} \left| S_{IJ} \left| M_{ij,J,ij'} \right|^2 \right.,
$$

where the sum is over initial partial waves with angular momenta, $J$, and final vibrational, $v'$, and rotational, $J'$, quantum numbers, $S_{IJ}$, $M_{ij,J,ij'}$, are the appropriate line strengths.

### Table 1

The 18 $C_2$, Singlet, Triplet, and Quintet Electronic States Formed During the Collision of Two Ground-state Carbon Atoms

| State     | $T_e$ (cm$^{-1}$) | $C_5$ | $C_6$ | $C_7$ |
|-----------|-------------------|-------|-------|-------|
| $X^1\Sigma^+_g$ | 0.0               | 21.81 | 5     | 40.9  |
| $A^1\Pi_n$    | 8312.4            | 0     | 0     | 46.29 |
| $B^1\Delta_n$ | 11895             | 3.635 | 3.635 | 46.29 |
| $B^1\Sigma^+_g$ | 15205            | 0     | 16    | 40.29 |
| $C^1\Pi_n$    | 34231             | -14.54| -13.49| 40.29 |
| $c^3\Sigma^+_u$ | 39500             | 0     | ...   | ...   |
| $a^3\Pi_m$    | 678.74            | -14.54| -14.54| 46.29 |
| $b^3\Sigma^+_g$ | 6254.9            | 0     | 0     | 40.9  |
| $c^3\Sigma^+_u$ | 9157.5            | 21.81 | 5     | 40.9  |
| $d^3\Pi_n$    | 20031             | 0     | 0     | 46.29 |
| $2^3\Sigma^+_u$ | 40042            | 0     | 0     | 40.9  |
| $l^3\Delta_n$ | 41889             | 3.635 | 8     | 46.29 |
| $1^1\Pi_n$    | 30165             | -14.54| -13.49| 40.9  |
| $1^3\Sigma^+_u$ | 40197            | 0     | 0     | 40.9  |
| $1^3\Pi_n$    | 51897             | 0     | 0     | 46.29 |
| $2^3\Pi_n$    | 64088             | 21.81 | 12    | 40.29 |
| $1^3\Delta_n$ | 49900             | 3.635 | ...   | ...   |
| $1^3\Sigma^+_u$ | ...              | 0     | ...   | ...   |

Notes. In column 2, the values of the term energies, $T_e$, are listed for the potential energies fit to Equation (1), relative to the minimum of the $X^1\Sigma^+_g$ potential energy. For each electronic state used in the present work, we list in atomic units values of $C_5$ from Boggio-Pasqua et al. (2000) and the adopted values of $C_3$ and $C_6$ entering Equation (1). The states $1^3\Sigma^+_u$, $1^3\Delta_n$, and $1^3\Sigma^+_g$ were not fitted in the present work, so we list the values of $T_e$ as calculated ab initio for $1^3\Sigma^+_u$ and $1^3\Delta_n$, while $1^3\Sigma^+_g$ is repulsive.

$^a$ Present calculations.

$^b$ Singlet and triplet values from Boggio-Pasqua et al. (2000); quintet values by symmetry. See the text for details.

$^c$ Actual value used. See the text for details.

$^d$ Estimated from Miller & Kelly (1972) or Chang (1967). See the text for details.
(Cowan 1981; Curtis 2003) or Hönl–London factors (Watson 2008), 137.036 is the speed of light in atomic units, \( \mu \) is the reduced mass of the collision system, and \( M_{\lambda E, J^g f^g} \) is given by the integral

\[
M_{\lambda E, J^g f^g} = \int_0^\infty F_{\lambda E J} (R) D_{g^g f^g} (R) \Phi_{J^g f^g} (R) dR.
\]

The wave function \( \Phi_{J^g f^g} (R) \) is a bound-state wave function of the final electronic state, \( F_{\lambda E J} (R) \) is an energy-normalized continuum wave function of the initial electronic state, and \( D_{g^g f^g} (R) \) is an electric dipole TDM between \( i \) and \( f \).

Due to presence of identical nuclei and the absence of nuclear spin in \( ^{12}\text{C}_2 \), the rotational quantum numbers of the \( ^{1}\Sigma_{g}^+ \) states are even, and those of the \( ^{1}\Sigma_{e}^+ \) states are odd and for any given value of \( \Lambda = 1 \) or 2, only one lambda-doubling level is populated (Amiot 1983). Thus, the statistical weight factor \( P_i \) is given by

\[
P_i = \frac{(2S_i + 1)}{81},
\]

where \( S_i \) is the total spin of the initial molecular electronic state (here 1, 3, or 5), and there are for two C(3\( ^3 \)P) atoms \( 3^4 = 81 \) molecular states labeled by \( \Lambda \) and \( S \). Thus, for example, for the \(^{12}\text{C}_2 \) molecule considered here, \( P_i = \frac{3}{81}, \frac{3}{81}, \frac{5}{81} \) respectively, for \( i = \Lambda^3 \Pi^u, b^3 \Sigma_e^+ , \) or \( \Lambda^5 \Pi^u \).

The bound and continuum state wave functions may be computed from their respective Schrödinger equations using the grid-based approach of the Numerov method (Cooley 1961; Johnson 1977), where we used step sizes of up to 0.001 Bohr. For example, for the X \(^{1}\Sigma_g^+ \) state, we find 55 vibrational levels and \( J = 0, 2, \ldots, 174 \), though not all levels will contribute to the cross sections. A finely spaced energy grid is required to account for resonances. In Figure 6, results are shown for the R. A. cross section as a function of energy for the singlet, triplet, and quintet transitions listed in Table 2. We plot the cross sections with the statistical factor \( P_i \) set equal to unity for all states. Numerous shape resonances are visible. For the \( ^3\Delta_u - ^3\Pi_g \) and \( ^3\Pi_g - ^3\Pi_u \) cross sections, resonance tunneling features are visible, corresponding to potential barriers (local maxima) in the entrance channels. The local maxima from the PECs are 0.015 eV at \( R = 6 \) for \( ^3\Delta_u \) 0.37 eV at \( R = 3.6 \) for \( ^2\Sigma_g^+ \), and 0.42 eV at \( R = 3.5 \) for \( ^3\Pi_u \) and as seen in Figure 6, the corresponding cross sections sharply diminish for collision energies below these values. Note that the cross sections for Deslandres-d’Azambuja transitions (\( \text{C}^2\Pi_g - \text{A}^1\Pi_u \)) dominate the other cross sections for all collision energies, followed by the cross sections for the Swan (\( \text{d}^3\Pi_g - \text{a}^3\Pi_u \)) transitions. The cross sections for Radi-Bornhauser transitions (\( ^1\Pi_u - ^1\Pi_g \)) rise sharply as the relative energy increases. The other cross sections are at least an order of magnitude weaker than those corresponding to Deslandres-d’Azambuja, Swan, and Radi-Bornhauser transitions, and will not contribute significantly to the total cross section. While the \( ^1\Pi_u \) state does support some bound levels (Bornhauser et al. 2017), the calculated cross sections from the \( ^2\Sigma_g^+ - ^1\Pi_u \) state are negligible because of the steeply repulsive tail of the initial \( ^2\Sigma_g^+ \) electronic state.

### 3.1. Rate Constant

The PECs and TDMs were then used to calculate the cross sections and rates for R.A. in the \(^{12}\text{C}_2 \) molecule. The thermal rate constant (in cm\(^3\) s\(^{-1}\)) at a given temperature \( T \) to form a...
molecule by R.A. is given by
\[
k_{i \rightarrow f} = \frac{8}{\mu \pi} \frac{1}{(k_B T)^{3/2}} \int_0^{\infty} E \sigma_{i \rightarrow f}(E) e^{-E/k_B T} dE, \tag{5}
\]
where \(k_B\) is Boltzmann’s constant.

The complicated resonance structures make it challenging to calculate accurately the rate coefficient using numerical integration (Bennett et al. 2003; Gustafsson et al. 2012). As a guide, the relationship \(v \sigma_{i \rightarrow f}^{QM}\), where \(v = \sqrt{2E/\mu}\), is used to designate an effective energy-dependent rate coefficient, where \(R(E)\) for a transition from state \(i\) to state \(f\) is given by
\[
R(E) = \sqrt{2E/\mu} \sigma_{i \rightarrow f}^{QM}(E). \tag{6}
\]

This form is often used to define a quasi-rate coefficient rather than one averaged over a Maxwellian distribution and was utilized in ultra-cold collisional studies (Krems et al. 2010; McLaughlin et al. 2014). In Figure 7, results are shown for the R.A. rates \(R(E)\) (in \(\text{cm}^3 \text{s}^{-1}\)) as a function of energy expressed in temperature units (K) for the cross sections calculated for the \(C_2\) molecule. The Deslandres-d’Azambuja \((C^1\Pi_g \rightarrow A^1\Pi_u)\) transitions are the main contributors for low temperature, and the Radi-Bornhauser \((1^3\Pi_u \rightarrow 1^3\Pi_g)\) bands are the main contributors for high temperatures. The Swan \((d^3\Pi_g \rightarrow a^3\Pi_u)\) bands also contribute to the total rate.

In Figure 8 we compare our Maxwellian averaged quantal rates for the dominant Deslandres-d’Azambuja, Swan, and Radi-Bornhauser transitions and their sum with those determined from the previous semiclassical approximation by Andreazza & Singh (1997) over the temperature range 100–10,000 K. The quantal rates have the appropriate statistical population included, so a comparison could be made directly with the previous semiclassical results of Andreazza & Singh (1997). The total rate coefficient is fit to better than 6 percent by the function
\[
\alpha(T) = 5.031 \times 10^{-18} + 1.501 \times 10^{-16}T^{-1}
+ 2.517 \times 10^{-2}T - 1.89 \times 10^{-25}T^2 \quad \text{cm}^3 \text{s}^{-1},
\quad 100 \leq T \leq 10,000 \text{ K}. \tag{7}
\]

Contemporary discussions of resonances in R.A. cross sections were given by, for example, Bennett et al. (2003), Barinovs & van Hemert (2006), Bennett et al. (2008), Augustovičová et al. (2012), Mrugała & Kraemer (2013), and Golubev et al. (2013), though earlier researchers also considered the problem in detail (Giusti-Suzor et al. 1976; Flower & Roueff 1979; Graff et al. 1983), with considerations of radiative and tunneling contributions to resonance widths. Our procedures for calculating the cross sections, e.g., Equation (2), and the corresponding rate coefficients, as shown in Figure 8, include shape and resonance tunneling resonances. Procedures for the precision treatment of the effects of radiative decay have been developed: (i) excise certain resonances from the cross sections, recalculate them including the sum of the partial widths for radiative decay and tunneling, and then insert them back; (ii) add the separately calculated resonance cross
sections to the semiclassical cross sections; or (iii) add the separately calculated resonance cross sections to a background smooth baseline derived from the quantum cross sections. Franz et al. (2011) and Antipov et al. (2013) examined R.A. of carbon and oxygen to form CO (A1Π–X1Σ+), where there is a local maximum in the A1Π state of 0.079 eV (900 K effective temperature). Previous calculations of rate coefficients corresponding to semiclassical cross sections (using different molecular data) were available for comparison (Dalgarno et al. 1990; Singh et al. 2002). Using the quantum mechanical theory (our Equation (2)) along with semiclassical methods, and with specific treatment of resonances, Franz et al. (2011) and Antipov et al. (2013) found that for the rate coefficients corresponding to quantum cross sections with Equation (2) (Franz et al. 2011) or to hybrid calculations using procedure (ii) (semiclassical theory combined with additive quantum treatment of resonances) (Antipov et al. 2013) that resonances contribute below about 900 K. However, the rate coefficients for the quantum calculation (Figure 2 of Franz et al. 2011) and those for the hybrid calculations (Figure 4(a) of Antipov et al. 2013), do not deviate until the temperature is below 100 K. Precision treatment of radiative decay for the numerous resonances in our cross sections might yield enhanced values at lower temperatures, but given the application envisioned, namely to calculate corresponding rate coefficients for applications to the chemical models of supernovae ejecta, where many chemical reactions enter and few reaction rate coefficients are known precisely and where the temperatures of interest are perhaps of order 1000–2000 K, the present procedures are satisfactory.

4. Discussion

We see that our present quantal rates are larger than those from the previous semiclassical results of Andreazza & Singh (1997) at temperatures below 7000 K, and our quantal rates persist with a value of about 7 × 10−18 cm3 s−1 as temperatures approach 100 K. Andreazza & Singh (1997) listed the Swan and Deslandres-d’Azambuja transitions (in that order) as the leading contributors to the R.A. process. Our results indicate that the Deslandres-d’Azambuja transitions dominate the Swan transitions for all temperatures. Andreazza & Singh (1997) used a potential energy function for the C1Πg state with a barrier of 0.002 eV; they did not list the cross sections, but in the semiclassical method the cross sections for C1Πg–A1Σg transitions would be negligible for relative energies less than effective collisional temperature of the barrier, about 25 K, so this would not affect the comparison at thermal temperatures. We note that Andreazza & Singh (1997) did not include quintet states (for which no experimental data were available at that time) and except for the trend toward lower temperatures, our total rate coefficient is in reasonable agreement with their calculation. We note that the 15Πg−15Πu transition is the main contributor (as seen from Figure 8) to the rate coefficient for temperatures above 5000 K.

As mentioned above, in laboratory carbon vapors generated by laser radiation, the presence of dicarbon is confirmed by, primarily, radiation from the Swan bands, but also from the Deslandres-d’Azambuja bands (Savastenko & Tarasenko 2011). In light emission from laser-induced expansion of carbon vapor from a graphite rod, Monchicourt (1991) found evidence of associative collisions of two ground-state carbon atoms.
However, the operative source of dicarbon depends on factors such as temperature and distance from the graphite substrate, and there is evidence that dicarbon is formed by dissociation from the graphite (Iida & Yeung 1994) or recombination through three-body reactions (Savastenko & Tarasenko 2011).

Recent modeling at certain densities of laser-induced plasmas using local thermal equilibrium and equations of states indicates C₂ may form in plasmas of Si, N, or Ar and C at characteristic temperatures roughly less than 5000 K (Shabanov & Gornushkin 2015), corresponding to the
relatively low temperature region of the plasma (De Giacomo & Hermann 2017). That dicarbon is formed by a recombination process involving two carbon atoms in laser-induced plasma chemistry was shown experimentally using carbon isotopes by Dong et al. (2013).

The dominance of the $1^5\Pi_g-1^5\Pi_u$ transitions in our calculations is interesting in light of theories of dicarbon formation in laser plasmas. In particular, Little & Browne (1987) theorized that the $d^3\Pi_g$ (v = 6) band of dicarbon is populated by recombination collisions of atomic carbon, possibly in the presence of a third body, through the $1^3\Pi_g$ state (see Caubet & Dorthe 1994). Subsequently, Bornhauser et al. (2011) experimentally verified that the metastable $1^3\Pi_g$ state perturbs the $d^3\Pi_g$ state (Bornhauser et al. 2015); population of the $1^3\Pi_g$ state leads to Swan (v = 6) fluorescence. Subsequent experiments demonstrated the existence of the $1^3\Pi_u$ state (Bornhauser et al. 2015). Depending on the densities and applicable chemistries of laser generated carbon vapors, the R.A. process $1^3\Pi_g-1^3\Pi_u$ might contribute to the production of dicarbon in the $1^3\Pi_g$ state enhancing the mechanism of Little & Browne (1987).

For models of carbonaceous dust production in core-collapse supernovae, the present results provide improved rates for an initial step in carbon chain production. Our results may be compared with rates from a kinetic theory based nucleation model (Lazzati & Heger 2016), which are a factor of 10⁶ larger, and can be applied to molecular nucleation models (Sluder et al. 2018) or chemical reaction network models (Yu et al. 2013; Clayton & Meyer 2018).

5. Conclusions

Accurate cross sections and rates for the formation of dicarbon by the R.A. process were computed for transitions from several excited electronic states using new ab initio potentials and TDM functions. Where calculated values exist in the literature, our TDM functions are in good agreement with previous results, but our calculations are presented over a more extensive range of internuclear distances. We also present TDM functions for the $B^1\Delta_g-A^1\Pi_u$ and $d^3\Pi_g-\Delta^3\Sigma_u^-$, $1^3\Sigma_g^-\Pi_1^\delta$ (Radi-Bornhauser band), $1^3\Sigma_g^-\Pi_3^\delta$, $2^3\Sigma_g^-\Pi_3^\delta$, $1^3\Delta_u$ and $1^3\Delta_g$ transitions, substantially extending the available TDM data for dicarbon. We found that at the highest temperatures, the quintet state Radi-Bornhauser ($1^3\Pi_g-1^3\Pi_u$) transitions are the dominant channel for R.A., followed by the Deslandres-d’Azambuja (C$^3\Pi_g$-A$^3\Pi_u$) transitions and Swan ($d^3\Pi_g$-A$^3\Pi_u$) transitions, while at lower temperatures the Deslandres-d’Azambuja transitions are dominant. The computed cross sections and rates for C$_2$ are suitable for applicability in a variety of interstellar environments including diffuse and translucent clouds and ejecta of core-collapse supernovae. In addition, our calculations do not contradict evidence that in laser ablated vapors dicarbon formation proceeds through the $1^3\Pi_g$ state. We concur with Furtenbacher et al. (2016) that further experimental studies on the Deslandres-d’Azambuja transitions are desirable.

This work was supported by a Smithsonian Scholarly Studies grant. B.M.McL acknowledges support by the US National Science Foundation through a grant to ITAMP at the Center for Astrophysics | Harvard & Smithsonian under the visitor’s program, the University of Georgia at Athens for the award of an adjunct professorship, and Queen’s University Belfast for a visiting research fellowship (VRF). We thank Captain Thomas J. Lavery, USN, Ret., for his constructive comments that enhanced the quality of this manuscript. The authors acknowledge this research used grants of computing time at the National Energy Research Scientific Computing Centre (NERSC), which is supported by the Office of Science of the U.S. Department of Energy (DOE) under contract No. DE-AC02-05CH11231. The authors gratefully acknowledge the Gauss Centre for Supercomputing e.V. (www.Gauss-center.eu) for funding this project by providing computing time on the GCS Supercomputer HAZELHEN at HZS Hochleistungsrechenzentrum Stuttgart (www.hlrs.de). ITAMP is supported in part by NSF Grant No. PHY-1607396.

ORCID iDs
James F. Babb https://orcid.org/0000-0002-3883-9501
R. T. Smyth https://orcid.org/0000-0002-4359-1408
B. M. McLaughlin https://orcid.org/0000-0002-5917-0763

References
Abellán, F. J., Indebetouw, R., Marcaide, J. M., et al. 2017, ApJL, 842, L24
A’Hearn, M. F., Millis, R. C., Schleicher, D. O., Osip, D. J., & Birch, P. V. 1995, Icar, 118, 223
Amiot, C. 1983, ApJS, 52, 329
Andreazza, C. M., Marinho, E. P., & Singh, P. D. 2006, MNRAS, 372, 1653
Andreazza, C. M., & Singh, P. D. 1997, MNRAS, 287, 287
Antipov, S. V., Gustafsson, M., & Nyman, G. 2013, MNRAS, 430, 946
Augustovičová, L., Špírko, V., Kraemer, W. P., & Soldán, P. 2012, CPL, 531, 59
Babb, J. F., & Dalgarno, A. 1995, PrRva, 51, 3021
Babb, J. F., & Kirby, K. P. 1998, in Molecular Astrophysics of Stars and Galaxies, ed. T W Hartquist & D A Williams (Oxford: Clarendon), 11
Babb, J. F., & McLaughlin, B. M. 2017a, JPhB, 50, 044003
Babb, J. F., & McLaughlin, B. M. 2017b, MNRAS, 468, 2052
Babb, J. F., & McLaughlin, B. M. 2018, ApJ, 860, 151
Barinovs, G., & van Hemert, M. C. 2006, ApJL, 636, 923
Bennett, O. J., Dickinson, A. S., Leininger, T., & Gadéa, F. X. 2008, MNRAS, 384, 1743
Bennett, O. L., Dickinson, A. S., Leininger, T., & Gadéa, X. 2003, MNRAS, 341, 361
Black, J. H., & Dalgarno, A. 1977, ApJS, 34, 405
Boggio-Pasqua, M., Voronin, A., Halvick, P., & Rayez, J.-C. 2000, J. Molec. Struct.: THEOCHEM, 531, 159
Bornhauser, P., Marquardt, R., Gourlaouen, C., et al. 2015, JChPh, 142, 094313
Bornhauser, P., Sych, Y., Knopp, G., Gerber, T., & Radi, P. P. 2011, JChPh, 134, 044302
Bornhauser, P., Visser, B., Beck, M., et al. 2017, JChPh, 146, 114309
Boschen, J. S., Theis, D., Ruedenberg, K., & Windus, T. L. 2014, Theor. Chem. Acc., 133, 1425
Brau, J. W., Testerman, L., Grevesse, N., et al. 1982, A&A, 108, 201
Brooke, J. S., Bernath, P. F., Schmidt, T. W., & Bacsak, G. B. 2013, JohnsQR, 124, 11
Bruna, P. J., & Grein, F. 2001, CaPh, 79, 653
Cairnie, M., Forrey, R. C., Babb, J. F., Stancil, P. C., & McLaughlin, B. M. 2017, MNRAS, 471, 2481
Caubet, P., & Dorthe, G. 1994, CPL, 218, 529
Chabalkowski, C. F., Peyerimhoff, S. D., & Buenker, R. J. 1983, CP, 81, 57
Chaffee, F. H., Jr., & Lutz, B. L. 1978, ApJL, 221, L91
Chang, T. Y. 1967, RvMP, 39, 911
Cherchneff, I., & Sarangi, A. 2011, in IAU Symp., The Molecular Universe, ed. J. Cernicharo & R. Bachiller (Cambridge: Cambridge Univ. Press), 228
Clayton, D. D. 2013, ApJ, 762, 5
Clayton, D. D., Deneault, E. A. N., & Meyer, B. S. 2001, ApJ, 562, 480
Clayton, D. D., Liu, W., & Dalgarno, A. 1999, Science, 283, 1290
Clayton, D. D., & Meyer, B. S. 2018, GeCoA, 221, 47
Cochran, A. L., Barker, E. S., & Gray, C. L. 2012, Icar, 218, 144
Cooley, J. W. 1961, Macom, 15, 363

The Astrophysical Journal, 876:38 (9pp), 2019 May 1
Babb, Smyth, & McLaughlin
