

THE RADIATIVE ASSOCIATION OF He^+ AND He AND H^+ AND H P. C. STANCIL,¹ J. F. BABB, AND A. DALGARNO

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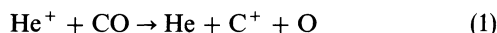
ABSTRACT

The rate coefficient for the radiative association of He^+ and He to form He_2^+ is determined for temperatures T between 20 K and 500,000 K. It can be represented by the relation $1.3 \times 10^{-21} T^{-0.008} \exp(-T/67) + 2.1 \times 10^{-24} T^{1.8} \exp(-T/22,800) \text{ cm}^3 \text{ s}^{-1}$ to within 25% applicable up to 50,000 K. It is about an order of magnitude less than the rate coefficient for the radiative association of H^+ and H to form H_2^+ . Cross sections for the He_2^+ and H_2^+ reactions calculated using a fully quantum-mechanical method reveal weak resonance features at low energies. Implications of the $\text{He}^+ + \text{He}$ radiative association process are discussed briefly in connection with the chemistry of supernova ejecta, planetary nebulae, and the early universe.

Subject headings: ISM: individual (NGC 7027) — molecular processes — supernovae: individual (SN 1987A)

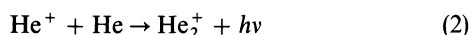
1. INTRODUCTION

The abundance of CO in the ejecta of supernova SN 1987A is controlled mainly through the level of element mixing and the dissociative charge exchange reaction

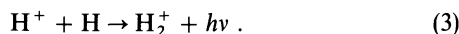


(Lepp, Dalgarno, & McCray 1990). Lepp et al. (1990) investigated chemical models incorporating a complete mixing of the ejecta constituents and predicted CO abundances two orders of magnitude less than what is observed due to the high efficiency of process (1). A partially unmixed model involving CO clumps surrounded by He can reproduce the observed abundances by adjusting the volume fraction of the unmixed gas (Liu, Dalgarno, & Lepp 1992).

Removal of He^+ through radiative recombination, charge exchange, and the radiative association process



can reduce the effectiveness of reaction (1). The rate coefficient for process (2) has not been previously calculated, though the process has been assumed in the models of Lepp et al. (1990) and Liu et al. (1992) to be unimportant. They took the rate coefficient to be approximately equal to the corresponding process for hydrogen



We present a calculation of the rate coefficient for the radiative association process (2) over a range of temperatures. The energy-dependent cross sections calculated using a fully quantum-mechanical method for reactions (2) and (3) are also presented.

2. THEORY

The direct radiative association of two atomic species to form a molecule can occur when the species approach with a relative energy E in an excited electronic state of the molecule. The species, initially in the vibrational continuum of the excited electronic state, decays to a bound vibrational-

rotational level of a lower bound electronic state through spontaneous emission thereby forming a molecule.

The initial state with momentum $\hbar k$ can be described as a superposition of partial waves characterized by the rotational angular momentum quantum number N , where $k^2 = 2\mu E/\hbar$ and μ is the reduced mass of the colliding system. The final vibrational-rotational levels are labeled by the vibrational quantum number v' and $N' = N \pm 1$. The photon energy $E_{\text{ph}} = h\nu = E + E_{v'N'}$, where ν is the photon frequency and $E_{v'N'}$ is the binding energy of the $v'N'$ level.

The quantum-mechanical radiative association cross section is given by (Zygelman & Dalgarno 1990)

$$\sigma(E) = \sum_N \sum_{v'} \sigma_N(v', E), \quad (4)$$

where

$$\sigma_N(v', E) = \frac{64}{3} \frac{\pi^5}{c^3} \frac{v^3}{k^2} p[NM_{v',N-1;k,N}^2 + (N+1)M_{v',N+1;k,N}^2] \quad (5)$$

and $M_{v',N';k,N}$ is the matrix element of the transition dipole moment $D(R)$ between the initial continuum wave function and the final bound vibrational-rotational wave function, R is the internuclear distance, and p is the probability of approach in the initial electronic state. For the systems considered here, He_2^+ and H_2^+ , the transition is from the first excited electronic state to the ground electronic state, $X^2\Sigma^+ \leftarrow A^2\Sigma^+$, and p is $\frac{1}{2}$. All equations are in atomic units unless otherwise noted.

Using the reduced masses $\mu(\text{H}_2^+) = 918.3263$ and $\mu(\text{He}_2^+) = 3647.8995$ and the appropriate constants, we may write equation (5) as

$$\sigma_N(v', E) = c_1(x) \frac{E_{\text{ph}}^3}{E} p[NM_{v',N-1;k,N}^2 + (N+1)M_{v',N+1;k,N}^2], \quad (6)$$

with $c_1(\text{H}_2^+) = 5.56845 \times 10^{-9}$ and $c_1(\text{He}_2^+) = 1.40182 \times 10^{-9}$.

The rate coefficient at a temperature T is given by

$$\alpha(T) = \left(\frac{8}{\mu\pi}\right)^{1/2} \left(\frac{1}{k_B T}\right)^{3/2} \int_0^\infty E \sigma(E) e^{-E/k_B T} dE \quad (7)$$

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or

$$\alpha(T) = c_2(x) T^{-3/2} \int_0^\infty E \sigma(E) e^{-E/k_B T} dE \text{ cm}^3 \text{ s}^{-1}, \quad (8)$$

where k_B is the Boltzmann constant, $c_2(\text{H}_2^+) = 5.72431 \times 10^{-2}$, and $c_2(\text{He}_2^+) = 2.87210 \times 10^{-2}$.

3. MOLECULAR DATA

3.1. Hydrogen Molecular Ion

We calculated the exact nonrelativistic Born-Oppenheimer potentials for the initial $A^2\Sigma_u^+$ and final $X^2\Sigma_g^+$ states using the code of Power (1973) and the $X \leftarrow A$ transition dipole moment using other methods out to an internuclear distance of 50. The results were checked using available tabulations (Madsen & Peek 1971; Ramaker & Peek 1973). Beyond $R = 50$, the long-range form of the potentials, $-\alpha_d/2R^4$, and the dipole moment, $\frac{1}{2}R$, were used. The dipole polarizability α_d is equal to 4.5 for hydrogen. The integration for the continuum wave function was carried out over the interval $R = 0.3$ to $R = 100$.

3.2. Helium Molecular Ion

The potentials of Metropoulos et al. (1992) were used between $R = 0.8$ and $R = 4$ for both the X and A states. Data between $R = 5$ and $R = 100$ as well as extrema and asymptotes for the two potentials were taken from the “uncorrected” curves of Ackermann & Hogreve (1991). Supplemental data for the ground state between $R = 6$ and $R = 15$ were taken from Metropoulos & Nicolaides (1991) and Bauschlicher, Partridge, & Ceperley (1989) and similarly for the excited state between $R = 4.6$ and $R = 6$ from Metropoulos, Nicolaides, & Buenker (1987). All of the above cited potentials were obtained using accurate ab initio multireference configuration-interaction (MRD-CI) methods and therefore justify the compilation. Additional short-range points between $R = 0.378$ and $R = 0.75$ from the early ab initio calculation of Gupta & Matsen (1967) were included in both states.

The long-range form was adopted from the model potential of Peach (1978) with the inclusion of the van der Waals term and is given by

$$V_L(R) = \mu' R^4 e^{-\lambda' R} - \frac{\alpha_d}{2R^4} - \frac{\alpha'_d}{2R^6} - \frac{C_6}{R^6}, \quad (9)$$

where C_6 is the van der Waals constant, which we calculated using the effective transition energies and oscillator strengths for He^+ and He given by Johnson, Epstein, & Meath (1967). The parameters α'_d , μ' , and λ' were determined by Peach (1978) and are reproduced in Table 1. The long-range form was matched to the ab initio data at $R = 12$.

The transition dipole moment data of Metropoulos et al. (1992) cover the interval from $R = 0.8$ to $R = 4$. They were extended to $R = 10$ using the results of McLaughlin et al. (1991). The Be^+ moment of 1.32, derived from data of Wiese, Smith, & Glennon (1966), was used at $R = 0$, the united atom limit. Beyond $R = 10$, the dipole moment has the long range form $\frac{1}{2}R$. As for the H_2^+ case, the integration over the continuum wave function extended from $R = 0.5$ to $R = 100$.

The $X^2\Sigma_u^+$ potential was tested by computing for $^3\text{He}^4\text{He}^+$ the frequencies of the $(v' = 1, N') \leftarrow (v' = 0, N' - 1)$ vibrational-rotational transitions and comparing them to the experimentally measured values of Yu & Wing (1987). The

TABLE 1
PARAMETERS USED IN THE LONG-RANGE
POTENTIAL OF He_2^+

| Parameter | Value |
|-------------------|------------------------|
| α_d | 1.38309 ^a |
| α'_d | 2.11380 ^b |
| C_6 | 0.374 ^c |
| $X^2\Sigma_u^+$ | |
| μ' | -0.314918 ^b |
| λ' | 2.12809 ^b |
| $A^2\Sigma_g^+$ | |
| μ' | 4.19449 ^b |
| λ' | 2.88960 ^b |

^a From Miller 1985.

^b From Peach 1978.

^c Determined using data of Johnson, Epstein, & Meath 1967.

discrepancy was within 4 cm^{-1} or 0.2% for all transitions. A similar comparison cannot be made for the $A^2\Sigma_g^+$ state since it is repulsive.

The ^4He nucleus has nuclear spin zero and obeys Bose statistics which require the total nuclear wave function to be symmetric. The nuclear spin wave function is symmetric. For the $X^2\Sigma_u^+$ state the nuclear coordinate wave function is symmetric for odd N' and antisymmetric for even N' . The even N' levels are unpopulated and since $N = N' \pm 1$ the sum in equation (4) is only taken over even N .

4. RESULTS

The radiative association cross sections $\sigma(E)$ given by equation (4) are shown in Figure 1 for reactions (2) and (3). The similarity in the shape of the cross sections is related to the potentials and transition dipole moments of the two systems. The ground states for both molecules are attractive with

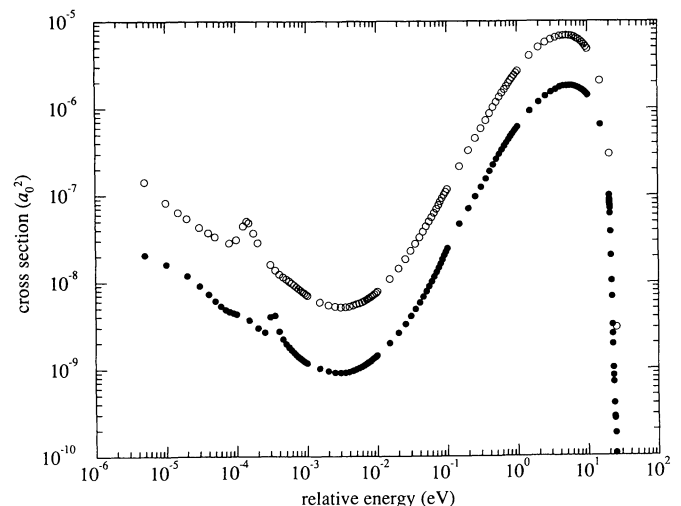


FIG. 1.—The cross sections for radiative association as a function of relative energy. Reaction (2), $\text{He}^+ + \text{He}$, is given by the filled circles, while reaction (3), $\text{H}^+ + \text{H}$, is given by the open circles.

minima near $R = 2$, while the excited states are essentially repulsive.

The maximum cross section occurs at a relative energy of 5.5 eV for both systems and is due to the large density of final vibrational-rotational states at energies corresponding to vertical transitions at the $R = 2$ minimum. The cross sections quickly drop for energies greater than about 10 eV as the bound vibrational-rotational states become inaccessible due to the vanishing Franck-Condon overlap. The cross section minimum occurs at 3 meV for both systems.

Enhancements occur at 0.14 meV and 0.34 meV for H_2^+ and He_2^+ , respectively. These are attributed to orbiting of the atomic species within a rotationally enhanced van der Waals well of the excited state. The difference in the energy of the features between H_2^+ and He_2^+ is related to the internuclear distance where the van der Waals minima occur: 12.55 and 8.85, respectively. For H_2^+ , the enhancement is caused primarily by the $N = 3$ barrier which contributes 66.7% of the total cross section at the resonance energy with some contribution from $N = 2$ (15.1%) and $N = 1$ (12.6%). About 58% of the cross section resonance arises from only four transitions originating from $N = 3$: $v' = 17, N' = 2$ (18.9%); $v' = 17, N' = 4$ (14.8%); $v' = 16, N' = 4$ (14.0%); and $v' = 16, N' = 2$ (10.2%). The major contributor for the He_2^+ enhancement is $N = 6$ (59.3%) with additional contribution from $N = 4$ (19.1%) and $N = 2$ (17.4%). The four major transitions, which originate from $N = 6$, are $v' = 21, N' = 5$ (14.9%); $v' = 21, N' = 7$ (7.5%); $v' = 20, N' = 5$ (11.5%); and $v' = 20, N' = 7$ (11.4%).

The cross sections are averaged over a Maxwellian velocity distribution as in equation (7) to give the rate coefficients. The results for He_2^+ , reaction (2), and H_2^+ , reaction (3), are shown in Figure 2 with some numerical values for He_2^+ given in Table 2. Our calculated rate coefficients for H_2^+ agree to within 3% with those given by Ramaker & Peek (1976). The rate coefficient for He_2^+ has a temperature dependence similar to H_2^+ , but it is approximately an order of magnitude less. Between 20 K and 50,000 K, it may be represented to within 25% by

$$\alpha_{\text{He}_2^+}(T) = 1.3 \times 10^{-21} T^{-0.008} \exp(-T/67) + 2.1 \times 10^{-24} T^{1.8} \exp(-T/22,800) \text{ cm}^3 \text{ s}^{-1}. \quad (10)$$

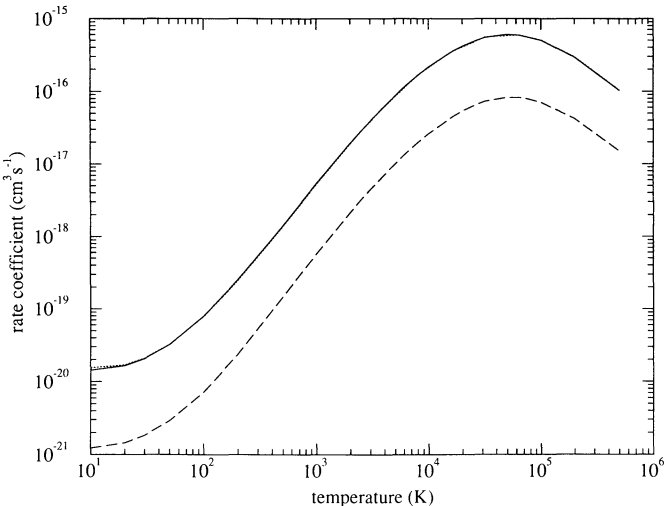


FIG. 2.—The rate coefficient for radiative associative as a function of temperature. The dash line is for reaction (2), $\text{He}^+ + \text{He}$, while the full line is for reaction (3), $\text{H}^+ + \text{H}$. The results of Ramaker & Peek (1976) are given as the dotted line for comparison.

| $T(\text{K})$ | $\alpha(T) \text{ cm}^3 \text{ s}^{-1}$ |
|---------------|---|
| 20..... | 1.44(−21) ^a |
| 30..... | 1.83(−21) |
| 50..... | 2.91(−21) |
| 100..... | 7.18(−21) |
| 200..... | 2.36(−20) |
| 500..... | 1.48(−19) |
| 1000..... | 5.82(−19) |
| 2000..... | 2.16(−18) |
| 2500..... | 3.22(−18) |
| 3000..... | 4.42(−18) |
| 4000..... | 7.13(−18) |
| 6000..... | 1.33(−17) |
| 8000..... | 1.98(−17) |
| 10000..... | 2.62(−17) |
| 16000..... | 4.39(−17) |
| 20000..... | 5.36(−17) |
| 25000..... | 6.34(−17) |
| 32000..... | 7.30(−17) |
| 50000..... | 8.29(−17) |
| 64000..... | 8.23(−17) |
| 100000..... | 7.11(−17) |
| 200000..... | 4.24(−17) |
| 500000..... | 1.51(−17) |

^a The notation 1.44(−21) corresponds to 1.44×10^{-21} .

The radiative association spectra for H_2^+ and He_2^+ at an energy of 0.75 eV are shown in Figure 3. The spectra appear in the near-infrared with maxima near $1.15 \mu\text{m}$. The lines are due to transitions to individual vibrational-rotational levels where the intensities are given by the partial cross section of equation (5). Spectra obtained at the energies of the orbiting features are

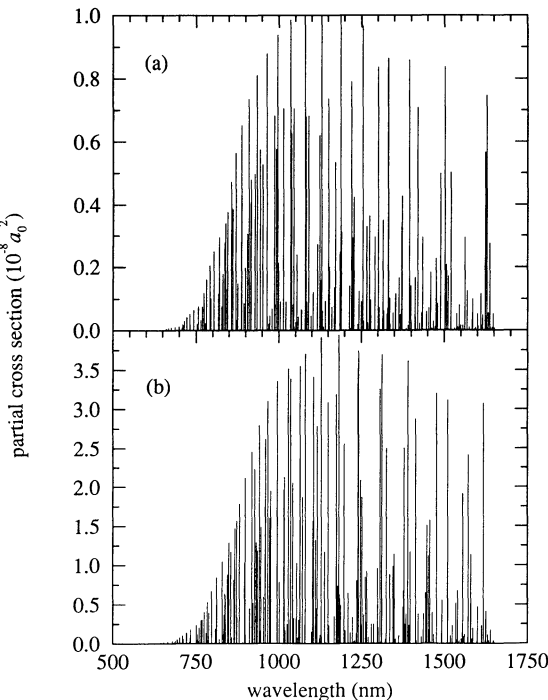


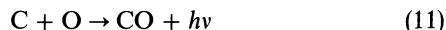
FIG. 3.—The spectrum of the radiative associative process at a relative energy of 0.75 eV. (a) Reaction (2), $\text{He}^+ + \text{He}$; (b) reaction (3), $\text{H}^+ + \text{H}$.

dominated by four lines in the infrared between 20 and 250 μm and arise from transitions to high vibrational levels as discussed above.

5. ASTROPHYSICAL IMPLICATIONS

5.1. SN 1987A

Lepp et al. (1990) presented a chemical model for the abundance of CO in SN 1987A. The radiative association process



is the major formation mechanism for CO while reaction (1) is the dominant CO-destruction process. The effectiveness of process (1) in removing CO is directly related to the density of He^+ , which can be destroyed through radiative recombination, charge exchange with neutral metals, and the radiative association reaction (2). Lepp et al. (1990) suggested that process (2) might reduce the effects of reaction (1), but our calculation shows that it is unimportant compared to other removal processes.

5.2. Planetary Nebulae

Cecchi-Pestellini & Dalgarno (1993) have investigated the emission of HeH^+ in planetary nebulae. They calculated the neutral distributions of H and He for various central star temperatures and then obtained the abundances of HeH^+ , H_2^+ , H_2 , and H^- versus the distance from the central source. They also obtained the abundances of these species for the planetary nebula NGC 7027 using the theoretical density and temperature structure model of Pequignot & Gruenwald (cf. Cecchi-Pestellini & Dalgarno 1993).

Using the rate coefficient of reaction (2) in the model of Pequignot & Gruenwald, we estimate that the maximum abundance of He_2^+ in NGC 7027 lies between 10^{-4} and 10^{-6} cm^{-3} at a radial distance of 0.0185 pc. In the model, He_2^+ is destroyed through dissociative recombination and charge transfer with H. The dissociative recombination rate coefficient is given by Mitchell (1990) to be between 10^{-8} and $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 300 K. We assumed a temperature dependence of $T^{-0.43}$. The value $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ was adopted for the charge transfer reaction with H. He_2^+ can also be destroyed by photodissociation, but the process is only important near the central source.

Figure 4 shows the abundance of He_2^+ as a function of the stellar distance. The abundance increases rapidly between 0.018 and 0.0185 pc due to a sharp drop in the electron density. For distances less than 0.018 pc, the electron density is greater

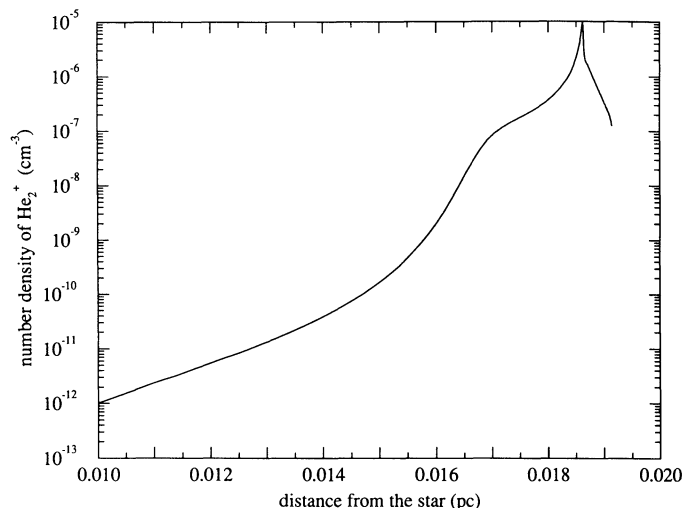


FIG. 4.—The predicted abundances of the helium molecular ion He_2^+ for the planetary nebulae NGC 7027 as a function of the distance from the central star.

than the neutral He or H densities and dissociative recombination is the dominant He_2^+ destruction mechanism. Beyond 0.0185 pc, the He_2^+ density decreases due to charge transfer with neutral H which is abundant near and outside the Strömgren radius. The maximum abundance occurs when the two destructive processes have equal rates. The prospect of detecting He_2^+ is negligible due to a small column density of only 10^9 cm^{-2} and the absence of allowed vibrational-rotational transitions.

5.3. The Early Universe

The process of radiative association will lead to the formation of the molecular ion He_2^+ at an earlier time in the evolution of the early universe than for H_2^+ . However, its formation seems not to have any interesting consequences. The chemical bond will be broken by any of photodissociation, dissociative recombination, or charge transfer.

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