Radiative Charge Transfer between the Helium Ion and Argon

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Abstract

The rate coefficient for radiative charge transfer between the helium ion and an argon atom is calculated. The rate coefficient is about 10^{-14} cm^3 s^{-1} at 300 K in agreement with earlier experimental data.

Key words: ISM: abundances – ISM: individual objects (Crab Nebula) – molecular processes

1. Introduction

The molecular ion 36ArH+ (argonium) was identified through its rotational transitions in the submillimeter wavelengths toward the Crab Nebula using SPIRE on board the Herschel Space Observatory (Barlow et al., 2013), with earlier and later observations revealing 38ArH+ and 39ArH+ in the diffuse interstellar medium using Herschel/HIFI (Schilke et al., 2014). With the ALMA Observatory, the redshifted spectra of ArH+ was detected in an external galaxy (Müller et al., 2015). Chemical modeling indicates that the presence of ArH+ may serve as a tracer of atomic gas in the very diffuse interstellar medium and as an indicator of cosmic-ray ionization rates (Müller et al., 2015; Neufeld & Wolfire, 2016).

Ar created in the supernova is predominately 36Ar and it was the isotope differences of 36ArH+ absorption spectra compared to 38ArH+ absorption spectra that provided the crucial clues leading to the initial identification in the Crab Nebula (Barlow et al., 2013). Recently, Priestley et al. (2017) modeled ArH+ formation in the filaments of the Crab Nebula, considering the specific high-energy synchrotron radiation found there, in addition to the cosmic-ray flux considered earlier for applications to the ISM. A detailed exploration of model parameters led Priestley et al. (2017) to the conclusion that in order to reproduce observed abundances the relevant cosmic-ray ionization rate is 10^7 times larger than the standard interstellar value, though sensitivity to other parameters, such as to the rate for dissociative recombination of ArH+, was noted.

In models of the Crab Nebula Ar+ ions are produced through cosmic-ray, UV and X-ray ionizations and by the reaction of H_2 with Ar (Jenkins 2013; Roueff et al., 2014). The ArH+ is formed by the ion–atom interchange reaction (Barlow et al., 2013)

\[ \text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H} \]  

and destroyed by reaction with H_2 (Barlow et al., 2013; Roueff et al., 2014). Sources of Ar+ that enter the chemical models were detailed by Schilke et al. (2014) and Priestley et al. (2017) and include photoionization of Ar and photodissociation of ArH+. Because He II is present in the Crab Nebula (Sankrit et al., 1998; Hester 2008), it is fitting to investigate whether an additional source of Ar+ might arise from charge transfer in Ar and He+ collisions. Previous studies (Smith et al. 1970; Isler 1974; Albat & Wirsam 1977) indicate that the direct charge transfer process

\[ \text{Ar}(^3\text{S}) + \text{He}^+(^2\text{S}) \rightarrow \text{Ar}^+(^3\text{P}^0) + \text{He}(1s^2\text{1S}) \]  

occurs through mechanisms involving couplings to excited molecular states that are inaccessible at thermal energies, and we conclude that charge transfer at thermal energies will proceed by the radiative charge transfer (RCT) mechanism

\[ \text{Ar} + \text{He}^+ \rightarrow \text{Ar}^+ + \text{He} + h\nu, \]  

where h\nu is the photon energy. Experimentally, the rate coefficient for the loss of helium ions in argon gas was found by Johnsen et al. (1973) to be no more than 10^{-13} cm^3 s^{-1} at 295 K, while Jones et al. (1979) found that the rate coefficient is greater than 2 \times 10^{-14} cm^3 s^{-1} at 300 K; both consistent with the early estimate of less than 10^{-13} cm^3 s^{-1} at 300 K (Fehsenfeld et al. 1966). Thus, (3) is likely to be relatively slow, but we are unaware of any detailed calculations for the cross sections and rate coefficients of (3).

2. Molecular Calculations

The molecular potential energy curve (PEC) of HeAr+ corresponding to the initial Ar(3S) atom and He+(1S) ion is the B 2Σ^+ state, which lies 8.225 eV (Stark & Peyerimhoff 1986) above the X 2Σ^+ and the A 2Π electronic states, which correlate to the final products Ar+(3P^0−3P^o) and He(1s^2\text{1S}) (see Figure 1). Calculations of the X 2Σ^+ and A 2Π PECs were given by Olson & Liu (1978), Gemein & Peyerimhoff (1990), and Staemmler (1990), the last two including fine structure for the A 2Π state, and the X 2Σ^+ and A 2Π states were calculated by Liao et al. (1987), using a relativistic CI method, and by Gemein et al. (1990) using the MRD-CI method. A summary of earlier calculations was given by Viehhage et al. (1991). Semi-empirical functions fitting the PECs are available (Siska 1986; Viehland et al. 1991). The B 2Σ^+ state has a well depth of about 0.17 eV (1375 cm^{-1}), while the X 2Σ^+ and A 2Π states have very shallow potentials wells of the order of tens of meV (Dabrowski et al. 1981; Liao et al. 1987; Viehland et al. 1991; Carrington et al. 1995). For the X 2Σ^+ state, the well depth is 286 cm^{-1}, while for the two states comprising the A 2Π (including fine structure) state the depths are \leq 182 cm^{-1}.

Depending on the relative magnitude of the transition dipole moments (TDMs) for the B 2Σ^+→X 2Σ^+ and B 2Σ^+→A 2Π transitions, qualitatively, we might expect a relatively large RCT rate coefficient because the B 2Σ^+ state is relatively shallow, the Franck–Condon overlap factors governing matrix
elements for transitions between the B $^3\Sigma^+$ state and between the A $^2\Pi$ state and the X $^3\Sigma^+$ state are favorable, and the net energy between the initial and final states is $\sim 8$ eV, which enters the transition probability as a cubic factor. To our knowledge, the TDMs coupling the B $^3\Sigma^+$ and X $^3\Sigma^+$ states and the B $^3\Sigma^+$ and A $^2\Pi$ states are not available in the literature, so we calculated them using the latest version of the quantum chemistry package MOLPRO, running on parallel computer architectures. The present results, described in more detail below, are shown in Figure 2. Inspection of the calculated TDMs indicates that the leading channel for RCT will be the B $^3\Sigma^+$–X $^3\Sigma^+$ transition in comparison to the B $^3\Sigma^+$–A $^2\Pi$ transition, similarly to the case of RCT between He$^+$ and Ne (Liu et al. 2010).

PECs and TDMs as a function of internuclear distance $R$ were calculated for a range of values of internuclear distance $R$ between 3 and 60 $a_0$. We used 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), in a similar manner to our recent molecular structure work on the HeC$^+$ and the CH$^+$ molecular complexes (Babb & McLaughlin 2017a, 2017b). The SA-MCSCF method is used as the reference wave function for the MRCI calculations. All the molecular data were obtained with MOLPRO 2015.1 (Werner et al. 2015) in the $C_{2v}$ Abelian symmetry point group using augmented—correlation—consistent polarized core-valence quintuplet basis sets (aug-cc-pCV5Z) for each atom/ion, in the MRCI+Q calculations (Helgaker et al. 2000). The use of large basis sets in molecular electronic structure calculations are well known to recover $\approx 98\%$ of the electron correlation effects.

In detail, for the HeAr$^+$ molecular cation, 13 molecular orbitals (MOs) are put into the active space, including seven $a_1$, three $b_1$, and three $b_2$ symmetry MOs. The rest of the electrons in the HeAr$^+$ system are put into the closed-shell orbitals. The MOs for the MRCI procedure are obtained from the SA-MCSCF method, where the averaging process was carried out on the lowest four $^3\Sigma^+$ ($^3A_2$), four $^3\Pi$ ($^3B_1$), and four $^3\Delta$ ($^3A_2$) molecular states of this molecule. We then use these 13 MOs ($7a_1$, $3b_1$, $3b_2$, $0a_2$), i.e., (7, 3, 3, 0), to perform all the PEC calculations of these electronic states in the MRCI + Q approximation as a function of bond length. The potential energies (PECs) and TDMs, respectively, are shown in Figures 1 and 2, for the restricted range $3 < R < 10 a_0$.

The long-range form of the $^3\Sigma^+$ state potential energy, correlating to He$^+$(X$^3\Sigma^+$)–Ar$^+$(X$^3\Sigma^+$), is (in atomic units)

$$V_b(R) \sim -\frac{1}{2}\alpha(\text{Ar})R^{-4} - \frac{1}{2}\alpha_q(\text{Ar})R^{-6} - C_6(\text{He}^+ \cdot \text{Ar})R^{-6},$$

(4)

where the electric dipole and quadrupole polarizabilities of Ar and the dispersion (van der Waals) constant of He$^+ \cdot$ Ar are, respectively, $\alpha(\text{Ar}) = 11.08$ (Kumar & Thakkar 2010), $\alpha_q(\text{Ar}) = 52.8$ (Jiang et al. 2015), and $C_6 = 2.36$. We calculated $C_6$ using the oscillator strength distributions (Babb 1994) of He$^+$ (Johnson et al. 1967) and of Ar (Kumar & Thakkar 2010). (The present value of $\frac{1}{2}\alpha_q(\text{Ar}) + C_6(\text{He}^+ \cdot \text{Ar}) = 28.8$, and is in good agreement with the value of 27.6 given by Siska 1986, who estimated $C_6$ using the Slater–Kirkwood approximation.)

The long-range forms of the X $^3\Sigma^+$ and A $^2\Pi$ states, correlating to He(1S$^1$S)$^+$(3P$^+$$^2P^0$), are (in atomic units)

$$V_{A,\lambda}(R) \sim -\frac{1}{2}\alpha(\text{He})R^{-4} - 8.64R^{-6},$$

(5)

where the electric dipole polarizability of He is $\alpha(\text{He}) = 1.383$ (Yan et al. 1996) and the term $O(R^{-6})$ is an estimate of the contribution of the electric quadrupole polarizability of helium and the dispersion constant for He$^+ \cdot$ Ar$^+$ (Siska 1986; Carrington et al. 1995). The TDMs are fitted to the form $R^{-12}$ for $R > 16 a_0$.

The calculated B $^3\Sigma^+$ potential gives a well of depth $D_0 = 0.03132$ eV (2526 cm$^{-1}$) at $R = 5 a_0$, to be compared to the experimentally determined well depth of 1375 cm$^{-1}$ at the same value of $R$ (Dabrowski et al. 1981). Part of this discrepancy may be due to our neglect of fine structure (spin–orbit coupling), as shown for the X $^3\Sigma^+$ and A $^2\Pi$ states by Staemmler (1990).
3. Cross Sections and Rate Coefficients

The radiative loss cross sections were calculated using the optical potential approach, which accounts for radiative loss in collisions of \( \text{He}^+ \) with \( \text{Ar} \). The theory is described in Babb & McLaughlin (2017b), see also, for example, Zygelman & Dalgarno (1988), Liu et al. (2009), and references therein. In carrying out the calculations of (3), the probability of approach in the \( B \ 2\Sigma^+ \) state is unity. The reduced mass of the colliding system corresponds to \( ^4\text{He} \) and \( ^{36}\text{Ar} \).

The calculated cross sections for radiative loss are shown in Figure 3. As expected, the \( B \ 2\Sigma^+ \) to \( X \ 2\Sigma^+ \) transition is significantly larger than the \( B \ 2\Sigma^+ \) to \( A \ 2\Pi \) transition. The radiative loss cross sections include the possibility of radiative association; however, because the well depth of the \( X \ 2\Sigma^+ \) state is only \( 262 \, \text{cm}^{-1} \) and the well depth of the \( A \ 2\Pi \) state is even less (Dabrowski et al. 1981; Carrington et al. 1995), and because the TDMs are diminished at the equilibrium distances characteristic of these states (about 5 \( \alpha_0 \)), the relative contributions of radiative association to radiative loss are assumed to be very small. Cross sections for loss through radiative association from the initial \( B \ 2\Sigma^+ \) state to bound levels of the \( B \ 2\Sigma^+ \) state are also insignificant compared to the cross sections given in Figure 3 because the transition probabilities depend on the de-excitation energies to the third power (Zygelman et al. 2014). Earlier detailed calculations on the LiHe\(^+\) system are illustrative (Dalgarno et al. 1996; Stancil & Zygelman 1996), in particular, Figure 2 of Augustovičová et al. (2012).

We therefore take the radiative loss cross section as a good approximation for the RCT cross section. This is in contrast to the HeNe\(^+\) system, where the well depth of the ground state is \( D_g = 6216 \pm 300 \, \text{cm}^{-1} \) and the TDMs (\( B \ 2\Sigma^+ \rightarrow X \ 2\Sigma^+ \) and \( B \ 2\Sigma^+ \rightarrow A \ 2\Pi \)) are comparable, with roughly equal contributions to radiative loss from RCT and from radiative association (Cooper et al. 1984; Liu et al. 2009). We note that cross sections for the various transitions that originate from the excited doublet electronic state of HeAr\(^+\) have Langevin \( 1/v \) or \( v^{-1/2} \), where \( v \) is the relative velocity (and \( E \) is the relative kinetic energy), background dependences at low energies, with overtaking resonance features. The rate coefficients for process (3) were calculated by averaging the cross sections for the \( B \ 2\Sigma^+ \rightarrow X \ 2\Sigma^+ \) transition over a Maxwellian velocity distribution. The results are given in Table 1.

| Temperature (K) | Rate Coefficient (cm\(^3\) s\(^{-1}\)) |
|-----------------|--------------------------------------|
| 77              | 1.05\((-14)\)                      |
| 100             | 1.05\((-14)\)                      |
| 200             | 1.01\((-14)\)                      |
| 300             | 9.86\((-15)\)                      |
| 400             | 9.69\((-15)\)                      |
| 500             | 9.56\((-15)\)                      |
| 600             | 9.48\((-15)\)                      |
| 700             | 9.39\((-15)\)                      |
| 800             | 9.32\((-15)\)                      |
| 900             | 9.28\((-15)\)                      |
| 1000            | 9.30\((-15)\)                      |
| 2000            | 8.89\((-15)\)                      |
| 3000            | 8.33\((-15)\)                      |

Note. Numbers in parentheses represent powers of 10 by which the preceding number should be multiplied.

Babb & McLaughlin

Figure 3. Cross sections in cm\(^2\) for radiative loss in collisions of \( \text{He}^+ \) with \( \text{Ar} \). Upper curve for \( B \ 2\Sigma^+ \rightarrow X \ 2\Sigma^+ \) transitions, lower curve for \( B \ 2\Sigma^+ \rightarrow A \ 2\Pi \) transitions.

4. Discussion

The calculated cross sections and rate coefficients are somewhat larger than those for RCT between He\(^+\) and Ne. For example, for RCT of He\(^+\) and Ne at 300 K, the experiment gives \( 1.0(3) \times 10^{-15} \, \text{cm}^3\,\text{s}^{-1} \) (Johnsen 1983) to be compared with the theoretical value of about \( 5 \times 10^{-16} \, \text{cm}^3\,\text{s}^{-1} \) (Cooper et al. 1984; Liu et al. 2009), while for RCT of He\(^+\) and Ar, we find a rate coefficient of \( 9.86 \times 10^{-15} \, \text{cm}^3\,\text{s}^{-1} \). Similarly, at 77 K, Johnsen (1983) measured a rate coefficient of \( \sim 2 \times 10^{-15} \, \text{cm}^3\,\text{s}^{-1} \) for RCT of He\(^+\) and Ne and Liu et al. (2009) calculate \( 3 \times 10^{-16} \, \text{cm}^3\,\text{s}^{-1} \), while at the same temperature for He\(^+\) and Ar we find a rate coefficient of 1.05 \( \times 10^{-14} \, \text{cm}^3\,\text{s}^{-1} \). The larger calculated values for the rate coefficients in the Ar system, compared to the calculated values for the Ne system, arise from two opposing effects. The dissociation limit of the \( B \ 2\Sigma^+ \) state is about \( 8.225 \, \text{eV} \) above the \( X \ 2\Sigma^+ \) state for HeAr\(^+\) and compared to about 3.125 \, \text{eV} \ for HeNe\(^+\), while the TDMs of the dominant \( B \ 2\Sigma^+ \) to \( X \ 2\Sigma^+ \) transition in HeNe\(^+\) (Cooper et al. 1984; Liu et al. 2009) is slightly larger than that for HeAr\(^+\).

However, the rate coefficient for process (3) is probably not large enough to be a significant factor in the production of ArH\(^+\) in the diffuse interstellar medium. The corresponding RCT reaction has been added to the chemical network relevant
to the ArH$^+$ molecular ion, as described in Neufeld & Wolfire (2016) in the PDLight version of the Meudon PDR code (Le Bourlot et al. 2012). The model was run both for diffuse galactic cloud conditions (standard interstellar radiation field, $n_H = 50$ cm$^{-3}$, $T = 50$ K, low visual extinction, cosmic ionization rate $\zeta = 10^{-16}$ s$^{-1}$) and for conditions corresponding to the Crab Nebula environment as reported in Priestley et al. (2017; $n_H = 2000$ cm$^{-3}$, $\zeta = 10^9$ s$^{-1}$). Using the value $10^{-14}$ cm$^3$s$^{-1}$ for the rate coefficient of the RCT reaction (3), no significant modifications of the chemical equilibrium of the ArH$^+$ molecular ion were found for either case.

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Software: molpro 2015.1, (Werner et al. 2015); PDLight, (Le Bourlot et al. 2012).

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References

Albat, R., & Wirsam, B. 1977, JPhB, 10, 81
Augustovičová, Ž., Špirko, V., Kramer, W. P., & Soldán, P. 2012, CPL, 531, 59
Babb, J., & McLaughlin, B. M. 2017a, MNRAS, 468, 2052
Babb, J., & McLaughlin, B. M. 2017b, JPhB, 50, 044003

Babb, J. F. 1994, MolPh, 81, 17
Barlow, M. J., Swinyard, B. M., Owen, P. J., et al. 2013, Sci, 342, 1343
Carrington, A., Leach, C. A., Marr, A. J., et al. 1995, JChPh, 102, 2379
Cooper, D. L., Kirby, K., & Dalgarno, A. 1984, CanJPh, 62, 1622
Dabrowski, I., Herzberg, G., & Yoshino, K. 1981, JMoSp, 89, 491
Dalgarno, A., Kirby, K., & Stancil, P. C. 1996, ApJ, 458, 397
Fehsenfeld, F. C., Schmeltekopf, A. L., Goldan, P. D., Schiff, H. I., & Ferguson, E. E. 1966, JChPh, 44, 4087
Gemein, B., de Vivie, R., & Peyerimhoff, S. D. 1990, JChPh, 93, 1165
Gemein, B., & Peyerimhoff, S. D. 1990, CPL, 173, 7
Helgaker, T., Jørgensen, P., & Olsen, J. 2000, Molecular Electronic-Structure Theory (New York: Wiley)
Hester, J. J. 2008, ARA&A, 46, 127
Isler, R. C. 1974, PhRvA, 10, 117
Jenkins, E. B. 2013, ApJ, 764, 25
Jiang, J., Mitroy, J., Cheng, Y., & Bromley, M. W. J. 2015, ADNDT, 101, 158
Johnsen, R. 1983, PhRvA, 28, 1460
Johnsen, R., Leu, M. T., & Biondi, M. A. 1973, PhRvA, 8, 1808
Johnson, R. E., Epstein, S. T., & Meath, W. J. 1967, JChPh, 47, 1271
Jones, J. D. C., Lister, D. G., & Twiddy, N. D. 1979, JPhB, 12, 2723
Kumar, A., & Thakkar, A. J. 2010, JChPh, 132, 074301
Le Bourlot, J., Le Petit, F., Pinto, C., Roueff, E., & Roy, F. 2012, A&A, 541, A76
Liao, M. Z., Balasubramaniam, K., Chapman, D., & Lin, S. H. 1987, CP, 111, 423
Liu, C. H., Qu, Y. Z., Wang, J. G., Li, Y., & Buenker, R. J. 2009, PhLA, 373, 3761
Liu, X. J., Qu, Y. Z., Xiao, B. J., et al. 2010, PhRvA, 81, 022717
Müller, H. S. P., Muller, S., Schilke, P., et al. 2015, A&A, 582, L4
Neufeld, D. A., & Wolfire, M. G. 2016, ApJ, 826, 183
Olson, R. E., & Liu, B. 1978, CPL, 56, 337
Priestley, F. D., Barlow, M. J., & Viti, S. 2017, MNRAS, 472, 4444
Roueff, E., Alekseyev, A. B., & Le Bourlot, J. 2014, A&A, 566, A30
Sankrit, R., Hester, J. J., Scowen, P. A., et al. 1998, ApJ, 504, 344
Schilke, P., Neufeld, D. A., Müller, H. S. P., et al. 2014, A&A, 566, A29
Siska, P. E. 1986, JChPh, 85, 7497
Smith, F. T., Fleischmann, H. H., & Young, R. A. 1970, PhRvA, 2, 379
Staemmler, V. 1990, ZPhyD, 16, 167
Stancil, P. C., & Zygelman, B. 1996, ApJ, 472, 102
Stärk, D., & Peyerimhoff, S. D. 1986, MolPh, 59, 1241
Viehland, L. A., Viggiano, A. A., & Mason, E. A. 1991, JChPh, 95, 7286
Werner, H.-J., Knowles, P. J., Knizia, G., et al. 2015, MOLPRO, version 2015.1, a package of ab initio programs, 2015, 1, Cardiff, UK, http://www.molpro.net
Yan, Z.-C., Babb, J. F., Dalgarno, A., & Drake, G. W. F. 1996, PhRvA, 54, 2824
Zygelman, B., & Dalgarno, A. 1988, PhRvA, 38, 1877
Zygelman, B., Lucic, Z., & Hudson, E. R. 2014, JPhB, 47, 015301

$^1$ Available at http://ism.obspm.fr.