

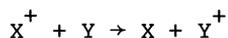
## ATOMIC AND MOLECULAR DATA

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Excitation, ionization and recombination processes are discussed elsewhere in this volume by Seaton (1977). I will restrict my attention to those processes involving heavy particles that may modify the ionization structure of planetary nebulae and that may affect the molecular composition of condensations and of the transition regions between the ionized nebulae and the surrounding interstellar gas.

### Charge transfer processes



may have important effects on the ionization structure of plasmas produced by ultraviolet and X-ray radiation. The process occurs through radial and rotational couplings of the adiabatic Born-Oppenheimer states that are formed by the approach of the interacting systems. At low velocities, rotational coupling is usually less important than radial coupling. The radial coupling matrix elements between adiabatic states with electronic eigenfunctions  $\Phi_i(\underline{r}|R)$  and  $\Phi_f(\underline{r}|R)$ , where  $\underline{r}$  represents the electron coordinates and  $R$  the internuclear separation, have the form  $\langle \Phi_i | \partial / \partial R | \Phi_f \rangle$ . If  $E_i(R)$  is the adiabatic interaction potential corresponding to  $\Phi_i$ , the radial coupling term may be written alternatively as  $\langle \Phi_i | \partial V / \partial R | \Phi_f \rangle / (E_i - E_f)$  where  $V$  is the electrostatic interaction. The effects of radial coupling are weak until velocities are reached where the collision time is of the order of the transition time  $\hbar / |E_i - E_f|$ . Thus charge transfer is improbable at thermal energies unless  $E_i - E_f$  approaches zero at some internuclear distance (cf. Hasted 1964).

The adiabatic interatomic potentials corresponding to the interactions of singly-charged positive ions and neutral atomic systems are highly specific and only rarely will the interaction potentials of the initial, final and any intermediate electronic states approach closely. A notable exception is the charge transfer reaction



for which the initial and final states approach closely at large and small separations. The reaction is almost resonant with energy defects of respectively 0.020 eV,  $-7 \times 10^{-5}$  eV and  $-8 \times 10^{-3}$  eV for  $\text{O}(^3\text{P}_J)$  in the  $J=2, 1$  and  $0$  fine-structure levels.

The importance of the reaction at thermal energies was first recognized in atmospheric physics where it is the major source of protons in the top-side ionosphere.

Laboratory measurements of (1) at ion impact energies  $E$  above 50 eV have been carried out by Stebbings et al. (1964) and of the reverse reaction at ion energies above 4 eV by Stebbings and Rutherford (1968). The measured cross sections  $Q$  can be reproduced by the expression

$$Q^{1/2} = a - b \log E \quad , \quad (2)$$

a form which is typical of symmetric resonance charge transfer processes (Dalgarno 1958).

Expression (2) was used by Rapp (1963) to derive a rate coefficient of  $8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at a temperature of  $1200^\circ\text{K}$ . Rapp argued further that the possible departure from (2) at thermal energies could reduce the rate coefficient by at most one order of magnitude. The extrapolation of the high energy data is consistent with the empirical rate coefficient of  $3.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at  $1200^\circ\text{K}$  derived by Hanson et al. (1963) from an analysis of the ion composition of the upper atmosphere.

More recently Fehsenfeld and Ferguson (1972) have measured the rate coefficient of the reverse of reaction (1) at thermal energies. They obtain a value of  $3.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at  $300^\circ\text{K}$ . For reaction (1) they derive a rate coefficient of  $6.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ .

In these studies, the populations of the fine structure levels of atomic oxygen are in thermal equilibrium either at  $300^\circ\text{K}$  or at  $1200^\circ\text{K}$ . In regions of low density, the  $^3\text{P}_0$  and  $^3\text{P}_1$  are depopulated and all the oxygen atoms are in the  $^3\text{P}_2$  ground state. Analyses that take account of the individual fine structure levels have been

presented by Field and Steigman (1971) and by Brown (1972). Field and Steigman adopted a statistical Langevin model which assumes that reaction occurs whenever the long range centrifugal barrier is surmounted (cf. Gioumousis and Stevenson 1958) and which partitions the energetically accessible exit channels according to their statistical weights (cf. Firsov 1962, Light and Lin 1965, Wolf 1966). Brown used a simplified two-state model in which the charge transfer probability depends upon the energy defect and the velocity. For the exothermic direction, the Langevin rate coefficient of Field and Steigman (1971) is independent of temperature whereas that of Brown (1972) increases with increasing temperature but the differences are not significant above 300°K.

The ion-molecule scheme for the formation of OH in diffuse interstellar clouds is initiated by



(Black and Dalgarno 1973, Watson 1973, Glassgold and Langer 1974) and empirical rate coefficients have been derived from the OH abundances measured towards  $\alpha$  Persei and  $\zeta$  Ophiuchi (Crutcher and Watson 1976, Snow 1976, Chaffee and Lutz 1977). The values depend upon the details of the cloud models. Crutcher and Watson (1976) obtain  $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  and Black and Dalgarno (1977)  $5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for the reverse of reaction (3).

The uncertainties do not permit a choice between the different models employed to describe the reaction but the laboratory, atmospheric and astrophysical data combine to support the view that the charge transfer reaction is rapid at the temperatures typical of planetary nebulae with a rate coefficient of about  $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  at  $10^4 \text{ K}$ . At  $10^4 \text{ K}$ , the reaction and its reverse are related by the ratio of the statistical weights so that in equilibrium the number densities satisfy

$$\frac{n(\text{O}^+)}{n(\text{O})} = \frac{8}{9} \frac{n(\text{H}^+)}{n(\text{H})}$$

(Chamberlain 1956).

The importance of the oxygen-hydrogen reactions in astrophysics appears to have been noted first by Chamberlain (1956) who discussed the OI/OII intensity ratios in the Cassiopeia radio source. Its effects on the ionization structure of planetary nebulae have been explored by Williams (1973).

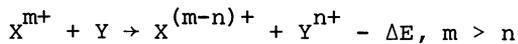
Steigman et al. (1971) have applied the statistical Langevin model to the charge transfer reaction



which is exothermic with an energy defect of 0.94 eV. At  $10^4$  K, they obtain a rate coefficient of  $5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for the forward reaction and of  $4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for the backward reaction. It appears however that the model is inappropriate and that the reaction proceeds through the close approach of the adiabatic  $4\Sigma^-$  and  $2\Pi$  molecular states which are weakly coupled by the spin-orbit interaction (Melius 1973). Melius has estimated a rate coefficient for (4) of about  $1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ .

No estimates are available at thermal energies for electron capture by  $\text{H}^+$  with any other systems of astrophysical interest. Each reaction will require individual study.

Because of the Coulomb repulsion between the positive ions in the final state, charge transfer of multiply-ionized atomic systems



is characterized by adiabatic interaction potentials that tend to intersect at some intermediate separation  $R_x$ , given approximately by  $R_x = (m-n)n/\Delta E$ . In practice adiabatic states of the same symmetry do not intersect and avoided crossings occur. The adiabatic interaction potentials follow the dashed curves illustrated schematically in figure 1.

The probability that during a collision crossing does take place depends upon the relative velocity and upon the energy separation  $\Delta E(R) = E_i(R) - E_f(R)$  between the adiabatic curves in the region of the avoided crossing at  $R_x$ .

Early analyses of the charge transfer reactions of multiply-ionized systems were carried out by Bates and Moiseiwitsch (1954), by Dalgarno (1954) and by Boyd and Moiseiwitsch (1957) using the Landau-Zener formula. Because of the restrictive conditions in which the assumptions that underly the formula are valid (Bates 1960, Mordinov and Firsov 1961, Nikitin 1961, 1962, Ovchinnikova 1964, Yagisawa 1976) it is an unreliable computational procedure for specific reaction rates but it is still useful as a guide to the

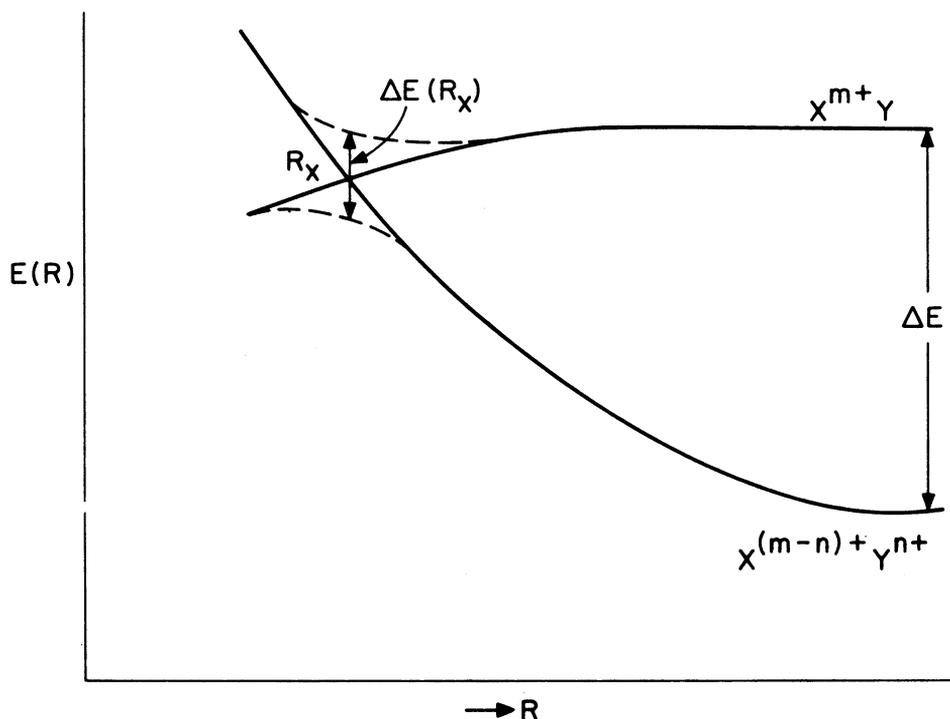


Figure 1: Adiabatic and diabatic interaction potentials

selection of those reactions that may be rapid at thermal energies and that should be studied by more sophisticated methods. The early discussions established the extreme sensitivity to  $\Delta E(R_x)$  and hence to  $R_x$ . Thus for the reaction



Bates and Moiseiwitsch (1956) calculated a rate coefficient of  $5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  at  $10^4 \text{ K}$ , a value confirmed recently by an elaborate two-state quantal study of McCarroll and Valiron (1976), whereas for

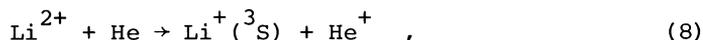


they obtained  $1 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$  and for

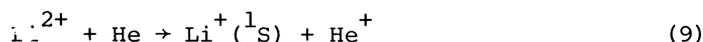


Boyd and Moisewitsch (1957) obtained  $7.2 \times 10^{-21} \text{ cm}^3 \text{ s}^{-1}$ .

The discussions established also the importance of scattering exit channels involving excited states. Thus for the reaction



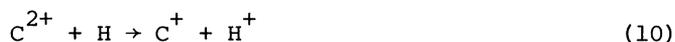
Dalgarno (1954) computed a rate coefficient of  $3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  at  $10^4 \text{ K}$ , and for the reaction



a rate coefficient of  $2 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ .

Laboratory measurements (cf. Hasted and Smith 1956, Hasted and Chong 1962, Spiers et al. 1972, Maier 1974) which show that some charge transfer reactions involving doubly-charged ions are rapid and some are not, consistent qualitatively with the wide range of cross sections suggested by the Landau-Zener formula.

Recently more elaborate calculations have been reported which are based upon accurate computations of the interaction potentials and which treat the collision aspects with two-state models of varying sophistication. McCarroll and Valiron (1975) have discussed the reaction



and have concluded that it is slow at thermal energies in disagreement with Steigman (1975a) who suggests that a rate coefficient exceeding  $1.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  is not unreasonable. Blint et al. (1976) have used a semi-classical analysis of the reaction



to calculate a rate coefficient of about  $10^{-9} \text{ cm}^3 \text{ s}^{-1}$  and Christiansen et al. (1977) have used an impact parameter model to derive a rate coefficient at  $10^4 \text{ K}$  of  $3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  for



Butler et al. (1977) have calculated accurate interaction potentials for  $\text{NH}^{2+}$  and it appears from them that



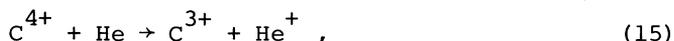
is probably rapid. The most sophisticated description of the scattering is that of McCarroll and Valiron (1976) which unlike the other studies took explicit recognition of the Coulomb character of the outgoing waves in the exit channel. Their results for reaction (5) happen to be close to the Landau-Zener calculations of Bates and Moiseiwitsch (1954).

The Landau-Zener formula asserts that reaction is improbable when  $[\Delta E(R_x)]^{1/2}/V$  is either small or large and the more detailed calculations suggest that for reactions to be rapid at thermal velocities  $R_x$  should be in the range between 3.5 and 7Å. Steigman (1975b) has drawn attention to the possible importance of charge transfer in limiting the abundances of highly-ionized systems in the intercloud medium (see also Weisheit 1973) and he has tabulated values of  $R_x$  for many cases of astrophysical interest. Most of the values are less than 3Å. However Steigman (1975b) restricted his considerations to reactions which terminate in the ground states of the product ions whereas charge transfer will often be dominated by transitions to excited product ions. A more comprehensive survey has been carried out by Butler and Dalgarno (1977) for the ions of C, N, O, Ne, Si, S, A and Fe interacting with atomic hydrogen and helium. Of the many cases, only the doubly-charged ions of carbon, oxygen, neon, sulphur and argon are unfavorable to charge transfer interactions with both hydrogen and helium.

In reactions with helium, double-charge transfer is possible (Steigman 1975b) and it may on occasion proceed more rapidly than single-charge transfer. An example is

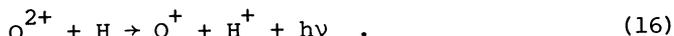


which is probably much more rapid than



for which no favorable crossing exists. Experimental evidence showing that double-charge transfer can dominate has been obtained for  $\text{C}^{4+}$ -He collisions at high energies (Crandall et al. 1976).

In the absence of a favorable crossing, charge transfer may proceed more rapidly if accompanied by the emission of a photon such as the process



The process involves the formation of a temporary molecule that radiates in an allowed electric dipole transition to some lower lying molecular state and its rate coefficient is much less sensitive to the details of the collision provided an attractive path for the approach of the interacting systems is available.

Semi-classical calculations (Bates 1951) have been carried out of radiative charge transfer with atomic hydrogen of the ions  $\text{He}^{2+}$  (Arthurs and Hyslop 1957),  $\text{He}^{+}$  (cf. Jura and Dalgarno 1971) and  $\text{C}^{2+}$ ,  $\text{C}^{3+}$  and  $\text{N}^{2+}$  (Butler et al. 1977). The radiative charge transfer of  $\text{He}^{2+}$  in He has also been studied (Allison and Dalgarno 1965). The rate coefficients are in the range of  $10^{-13}$  to  $10^{-15} \text{cm}^3 \text{s}^{-1}$ .

Emission of a photon during a collision may terminate in a bound state of the molecule and in low density gases radiative association is the major mechanism of molecular formation. Important examples are



(cf. Abgrall, Giusti-Suzor and Roueff 1976)



(Bates 1951, Ramaker and Peck 1976)



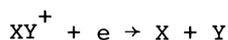
(Dabrowski and Herzberg 1976) and



(Jura and Dalgarno 1971).

Dabrowski and Herzberg (1976) have suggested that vibrationally excited  $\text{HeH}^+$  ions may be the source of the unidentified spectral features near  $3\mu$  observed in NGC 7027 (Merrill, Soifer and Russell 1975). If positive molecular ions do exist in nebulae, their vibrational levels will be rapidly populated by electron impact excitation, the cross sections for which are probably very large.

Positive molecular ions are usually rapidly removed by dissociative recombination



but  $\text{H}_2^+$ ,  $\text{CH}^+$  and  $\text{HeH}^+$  may be exceptions.

In regions of high electron density, the initiating radiative process leading towards molecular formation can be radiative attachment



to form  $\text{H}^-$  followed by the rapid process of associative detachment



Molecular hydrogen has been detected in NGC 7027 in the  $V=1$  vibrational level (Treffers et al. 1976) and Black (1977) has suggested that it is formed in the transition region by reaction (22) and then pumped by ultraviolet fluorescence (Black and Dalgarno 1976). Once  $\text{H}_2$  has been produced, other molecules may be created by a wide variety of ion-molecule and neutral atom-molecule chemical reactions (cf. Watson 1976, Dalgarno and Black 1976, Huntress 1977). Black (1977) has constructed a model of NGC 7027 and has predicted the abundances of several simple molecules.

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## References

- Allison, D. C. and Dalgarno, A.: 1965, *Proc. Phys. Soc.* **85**, 845.
- Arthurs, A. M. and Hyslop, J.: 1957, *Proc. Phys. Soc.* **A70**, 849.
- Bates, D. R.: 1951, *Mon. Not. Roy. Astron. Soc.* **111**, 303.
- Bates, D. R.: 1960, *Proc. Roy. Soc. A* **257**, 22.
- Bates, D. R. and Moiseiwitsch, B. L.: 1954, *Proc. Phys. Soc.* **A67**, 805.
- Black, J. H.: 1977, preprint.
- Black, J. H. and Dalgarno, A.: 1973, *Ap. J. Lett.* **184**, L101.
- Black, J. H. and Dalgarno, A.: 1976, *Ap. J.* **203**, 132.
- Black, J. H. and Dalgarno, A.: 1977, *Ap. J. Suppl.*, July 15, in press.
- Blint, R. J., Watson, W. D. and Christensen, R. B.: 1976, *Ap. J.* **205**, 634.
- Boyd, T. J. M. and Moiseiwitsch, B. L.: 1957, *Proc. Phys. Soc.* **A70**, 809.
- Brown, R. L.: 1972, *Astrophys. and Space Sci.* **16**, 274.
- Butler, S. E. and Dalgarno, A.: 1977, *Comments on Atomic and Molecular Physics*, in press.
- Butler, S. E., Guberman, S. L. and Dalgarno, A.: 1977, *Phys. Rev. A*, in press.
- Chaffee, F. H. and Lutz, B. L.: 1977, *Ap. J.* **213**, 394.
- Chamberlain, J. W.: 1956, *Ap. J.* **124**, 390.
- Crandell, D. H., Olson, R. E. Shipsey, E. J. and Browne, J. C.: 1976, *Phys. Rev. Lett.* **36**, 858.
- Christensen, R. B., Watson, W. D. and Blint, R. J.: 1977, *Ap. J.* **213**, 712.
- Crutcher, R. M. and Watson, W. D.: 1976, *Ap. J. Lett.* **203**, L123.
- Dabrowski, I. and Herzberg, G.: 1976, preprint.
- Dalgarno, A. and Black, J. H.: 1976, *Rep. Progr. Phys.* **39**, 573.
- Dalgarno, A.: 1954, *Proc. Phys. Soc.* **A67**, 1010.
- Dalgarno, A.: 1958, *Phil. Trans. Roy. Soc. A* **250**, 426.
- Fehsenfeld, F. C. and Ferguson, E. E.: 1972, *J. Chem. Phys.* **56**, 3066.
- Field, G. B. and Steigman, G.: 1971, *Ap. J.* **166**, 59.
- Firsov, O. B.: 1962, *Soviet Phys.-JETP* **15**, 906.
- Gioumousis, G. and Stevenson, D. P.: 1958, *J. Chem. Phys.* **29**, 294.
- Glassgold, A. E. and Langer, W.: 1974, *Ap. J.* **193**, 73.
- Hasted, J. B.: 1964, *Physics of Atomic Collisions* (Butterworth: London).
- Hasted, J. B. and Chong, A. Y. J.: 1962, *Proc. Phys. Soc.* **80**, 893.
- Hasted, J. B. and Smith, R. A.: 1956, *Proc. Roy. Soc. A* **235**, 349.
- Hanson, W. B., Patterson, T. N. L. and Degaonkar, S. S.: 1963, *J. Geophys. Res.* **68**, 6203.
- Huntress, W. T.: 1977, *Ap. J. Suppl.* **33**, 495.
- Jura, M. and Dalgarno, A.: 1971, *Astron. Ap.* **14**, 243.
- Light, J. C. and Lin, J.: 1965, *J. Chem. Phys.* **43**, 3209.
- Maier, W. B.: 1974, *J. Chem. Phys.* **60**, 3588.
- McCarroll, R. and Valiron, P.: 1975, *Astron. Ap.* **44**, 465.
- McCarroll, R. and Valiron, P.: 1976, *Astron. Ap.* **53**, 83.
- Melius, C. F.: 1973, *Abstracts of Papers VIII ICPEAC (Belgrade)* Ed. Čobić, B. C. and Kurepa, M. V.

- Merrill, K. M., Soifer, B. T. and Russell, R. W.: 1975, *Ap. J. Lett.* 200, L37.
- Mordinov, Yu. P. and Firsov, O. B.: 1961, *Soviet Phys.-JETP* 12, 301.
- Nikitin, E. E.: 1961, *Opt. Spectrosc.* 11, 246.
- Nikitin, E. E.: 1962, *Opt. Spectrosc.* 13, 431.
- Ovchinnikova, M. Ya.: 1964, *Opt. Spectrosc.* 17, 447.
- Ramaker, D. E. and Peek, J. M.: 1976, *Phys. Rev.* A13, 58.
- Rapp, D.: 1963, *J. Geophys. Res.* 68, 1773.
- Seaton, M. J.: 1977, This Volume.
- Snow, T. P.: 1976, *Ap. J. Lett.* 204, L127.
- Spears, K. G., Fehsenfeld, F. C., McFarland, M. and Ferguson, E. E.: 1972, *J. Chem. Phys.* 56, 2562.
- Stebbins, R. F. and Rutherford, J. A.: 1968, *J. Geophys. Res.* 73, 1035.
- Stebbins, R. F., Smith, A. C. H. and Ehrhardt, H.: 1964, *J. Geophys. Res.* 69, 2349.
- Steigman, G.: 1975a, *Ap. J. Lett.* 195, L39.
- Steigman, G.: 1975b, *Ap. J.* 199, 642.
- Treffers, R. R., Fink, U., Larson, H. P. and Gautier, T. N.: 1976, *Ap. J.* 209, 793.
- Watson, W. D.: 1973, *Ap. J. Lett.* 182, L73.
- Watson, W. D.: 1976, *Rev. Mod. Phys.* 48, 513.
- Weisheit, J. C.: 1973, *Ap. J.* 185, 877.
- Williams, R. E.: 1973, *Mon. Not. Roy. Astron. Soc.* 164, 111.
- Wolf, F. A.: 1966, *J. Chem. Phys.* 44, 1619.
- Yagisawa, H.: 1976, *J. Phys. B.* 9, 2757.

## DISCUSSION

Kaler: The  $N^+/O^+$  ratios in planetary nebulae are at a minimum for a central star temperature of about 40,000°K. Below this value,  $N^+/O^+$  rapidly increases; the O is apparently going neutral faster than the N which fits very nicely with your comments. Also, it is at this stellar temperature that He is becoming neutral. What is the charge transfer effect with regard to the neutral helium.

Dalgarno: My discussion included either hydrogen or helium. I didn't specify which I think is more probable, except in the case of double charge transfer.

Aller: The high charge exchange rate for  $Si^{++}$  is interesting because  $Si^+$  permitted lines are sometimes detected in nebulae of such high excitation where they would not be expected. Clearly, the production of  $Si^+$  ions must be favored.

Dalgarno: Charge transfer is into the ground state of  $Si^+$ . Charge transfer doesn't actually contribute to the emission of the silicon line.

Seaton: For planetary nebulae, one must compare charge exchange rates with electron recombination rates. If much longer, or much smaller, the exact value is not important (large charge exchange rates give ionization equilibrium proportional to statistical weights).