CHARGE EXCHANGE REACTIONS IN ASTROPHYSICAL PLASMAS

R. McCarroll
Laboratoire d'Astrophysique, Université de Bordeaux 1, France
P. Valiron
Groupe d'Astrophysique, Université de Grenoble 1, France
L. Opradolce
Instituto de Astronomia y Fisica del Espacio, Buenos Aires

ABSTRACT

A review is presented of charge exchange reactions of multiply charged ions with atomic hydrogen and helium at thermal-eV energies, typical of the physical conditions encountered in planetary nebulae. The basic features of the processes are analyzed in the framework of the molecular model of atomic collisions. A discussion is given of the different theoretical approaches to the calculation of the collision cross sections. A comparison with recent experimental data is included.

INTRODUCTION

An analysis of the emission line spectrum of the planetary NGC 7027 led Péquignot et al. (1978) to the conclusion that recombination of certain doubly and more highly charged ions takes place primarily by charge exchange with neutral hydrogen or helium. Assuming reasonable empirical estimates of the charge exchange reaction rates, Péquignot (1980a) obtained excellent agreement between the theoretical and observed emission fluxes produced by ions of C, N, O, Ne and S in both the visible and UV spectrum. These conclusions were amply confirmred by further investigation (Péquignot 1980b, Ulrich and Péquignot 1980) of other planetary nebulae (NGC 7662, 6720) and indeed of other similar objects such as the nebulae surrounding the Seyfert galaxies (NGC 3516).

Theoretical work on the physics of charge exchange reactions involving multiply charged ions by McCarroll and Valiron (1975, 1976, 1978, 1979), Christensen et al. (1977), Watson and Christensen (1979), Butler et al. (1980), Butler and Dalgarno (1980) and Gargaud et al. (1981, 1982) are in substantial agreement with the empirical rate coefficients proposed by Péquignot, at least for the stronger reactions with rate coefficients of the order of several 10^{-9} cm^3 s^{-1}. For weaker reactions the problem is more confused. For example, the case of charge exchange in O III/H collisions has a controversial history. Péquignot et al. require a rate coefficient of $\sim 8 \times 10^{-10}$ cm^3 s^{-1} to explain the observed O II line

187

intensities, in apparent discrepancy with the early prediction (1978) of $\sim 10^{-13} \text{cm}^3 \text{s}^{-1}$. However, later detailed calculations by Butler et al. (1980), taking account of the possibility of configuration mixing in the O III ionic core, yield a rate coefficient of $\sim 6\times10^{-10} \text{cm}^3 \text{s}^{-1}$, in good agreement with Péquignot. On the other hand, all theoretical considerations of charge exchange in Ne III/H and Ne III/He collisions (Dalgarno et al. 1980) agree that the reaction rate must be slow (or at least several orders of magnitude smaller than the value required by Péquignot to explain the observed data onNe II.

The existence of such exceptions suggests caution in pursuing an analysis with empirical rate coefficients too far. It is therefore of the utmost importance to dispose of reliable cross section data. Only then, can the observations be interpreted in a consistent way.

Some mention should also be made of the possibility of charge exchange as a possible ionization source in nebular gas. Typical charge exchange reactions of an A^{+q} ion with atomic hydrogen

$$A^{+q} + H \rightarrow A^{+q-1}(n) + H^+ \tag{1}$$

produces in most cases an ion A^{+q-1} in an excited state n. As a result, the inverse reaction is not usually of importance since the excited state decays rapidly by spontaneous radiative emission. However, if the reaction (1) can proceed via the ground state of A^{+q-1}, then the inverse process of charge transfer ionization can also occur easily. Baliunas and Butler (1980) have shown how the ionization equilibrium of Si is affected by this process. We may also expect a similar effect on the ionization equilibrium of Fe (Gargaud et al. 1982).

The aim of this review is not to give an exhaustive list of rate coefficients. Rather, it is to explain the underlying physical mechanisms of charge exchange in thermal collisions of multiply charged ions with atomic hydrogen or helium and to give some idea where we may expect new advances in the future. The advent of low energy ion sources (Phaneuf 1981, Huber 1982, Ohtani 1982) open up real possibilities of investigating important astrophysical reactions in the energy range from 10 eV upwards. Since the physical mechanism for charge exchange is essentially the same at all energies from thermal to several 100 eV, there is a real hope in the next few years that theory may be used to extrapolate experimental data down to the astrophysically interesting range of 0.01 - 10 eV.

PHYSICAL MODEL OF THE CHARGE EXCHANGE PROCESS

At thermal to eV energies, where the relative collision velocity is small compared with the characteristic orbital velocity associated with the valence electrons, the molecular model may be used to describe the charge exchange process. Let us consider for illustration reaction (1).

The entry channel $(A^{+q} + H)$ is attractive at large internuclear distances, due to the polarization potential $-\alpha q^2/2R^4$, where α is the polarizability of H and R is the internuclear distance. As a consequence there is no activation barrier and, if conditions are favourable, the cross section may become very large at thermal energies.

For $q > 2$, the exit channels $(A^{+q-1}(n) + H^+$ are dominated by the repulsive Coulomb potential $(q-1)/R_{+q}$ A curve crossing of the adiabatic potential energy curves of the $(AH)^{+q}$ molecular ion may be expected to occur at a value of R given by

$$\{(q-1)/R\} + \{q^2\alpha/2R^4\} = E_i - E_f = \Delta E(R) \qquad (2)$$

where E_i and E_f are respectively the internal energy of the initial and final reaction products. Of course, because of the Wigner non crossing rule, potential energy crossings between states of the same molecular symmetry are not allowed. As a result, many of the crossings predicted by (2) become avoided crossings. A typical illustration is given in figure 1, where are plotted the various molecular states involved in the charge exchange process in Ar VII/He collisions (Opradolce et al. 1982).
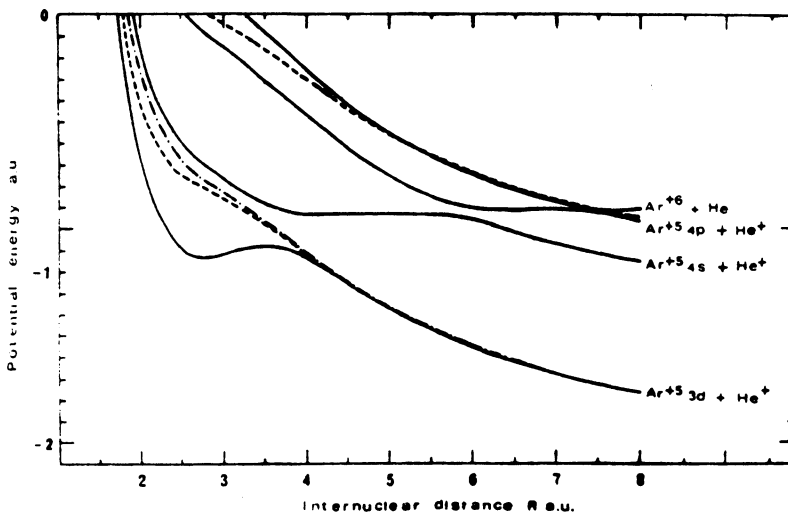

Fig. 1. Singlet potential energy curves of various adiabatic states of the molecular ion (ArHe)$^{+6}$ as a function of the internuclear distance. The solid curves refer to $^1\Sigma$ states, the dashed curves to $^1\Pi$ states and the chain curve to a $^1\Delta$ state. The dissociation products are as labelled.
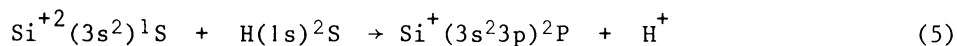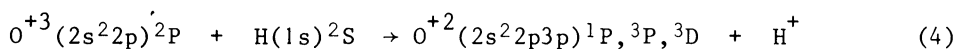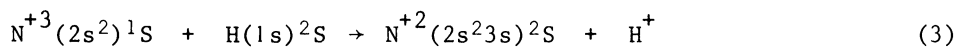
Since electronic transitions between molecular states occur to the breakdown of the Born-Oppenheimer approximation in the vicinity of the curve crossings, it is clear that charge exchange is a highly selective process. Firstly the reaction must be exergic, $E_i > E_f$, for otherwise

no curve crossing would occur. Secondly, the energy separation $\Delta E(R_x)$ at an avoided crossing located at R_x must be neither too large nor too small. If $\Delta E(R_x)$ is of the order of a few eV or greater, the transition probability is very small and adiabatic conditions prevail. If $\Delta E(R_x)$ is of the order of 10^{-2} eV or less, diabatic conditions prevail. As a general rule electronic transitions take place at low energies only when $0.1 < \Delta E(R_x) < 1$ eV. This condition is only satisfied for crossings which occur at intermediate internuclear distances ($4 < R_x < 10\ a_0$). At higher energies (> 1 keV/amu) these conditions are of course less restrictive since certain molecular states may then be strongly coupled over a wide range of internuclear distances rather than localized in the vicinity of the curve crossings.
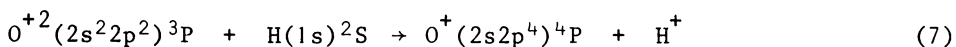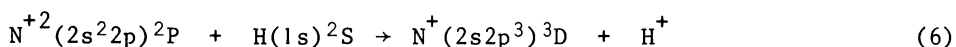
It is thus obvious from these simple considerations that charge exchange with highly charged ions takes place mainly via capture into excited Rydberg states. For ionic charge q of the order of 3, 4, capture into states with principal quantum number n = 3 is the most probable and the application of the molecular model is a feasible proposition. For higher q, when capture into Rydberg states with n > 5 becomes possible, the number of interacting molecular states may become exceedingly large; other methods (Janev 1982) are then to be preferred.

It is convenient to distinguish two types of processes (Butler and Dalgarno 1980).
Type I. Monoelectronic processes where electron capture takes place into an orbital (excited or not) without any change of the orbital configuration of the ionic core. Typical examples are

$$N^{+3}(2s^2)^1S + H(1s)^2S \rightarrow N^{+2}(2s^23s)^2S + H^+ \tag{3}$$

$$O^{+3}(2s^22p)^2P + H(1s)^2S \rightarrow O^{+2}(2s^22p3p)^1P, {}^3P, {}^3D + H^+ \tag{4}$$

$$Si^{+2}(3s^2)^1S + H(1s)^2S \rightarrow Si^+(3s^23p)^2P + H^+ \tag{5}$$

Type II. Two electron (or configuration mixing) processes, where electron capture into a valence orbital is accompanied by a rearrangement of the ionic core orbitals. Typical examples are

$$N^{+2}(2s^22p)^2P + H(1s)^2S \rightarrow N^+(2s2p^3)^3D + H^+ \tag{6}$$

$$O^{+2}(2s^22p^2)^3P + H(1s)^2S \rightarrow O^+(2s2p^4)^4P + H^+ \tag{7}$$

As a general rule, type II processes are important only when type I processes are weak. This is frequently the case for doubly charged ions when the type I processes are either too exoergic (R_x too small) or too endoergic (no curve crossing). In these cases, such as N III/H and O III/H, type II processes are the dominant ones. However, for a given value of R_x, type II processes are an order of magnitude weaker than type I processes.

POTENTIAL ENERGY CURVES

In the quasi-molecular model of charge exchange, the main problem resides in the determination of the potential energy curves of the molecular states correlated to the entry and all possible exit channels. For type I processes, the dominant processes for ions with q > 3, the electronic structure is that of a single electron in an excited state outside of the ground state configuration. Here, frozen Hartree-Fock and model potential methods work well (McCarroll and Valiron 1975, 1976, Christensen et al. 1977), though each method has its limitations. Hartree-Fock methods take no account of electron correlation and model potential potential methods do not allow for adjustments of the core configuration. However, model potential methods offer several advantages over ab-initio methods in that they guarantee the correct dissociation limits and long range interactions; these considerations are of vital importance in the investigation of reactions at eV energies. Neither approach can be expected to treat satisfactorily charge exchange reactions of type II, when more than one active electron is involved. Here, the use of a configuration interaction method is required (Dalgarno et al. 1980).

The critical parameters for charge exchange reactions are the position of the avoided crossings R_x and the energy differences $E(R_x)$ at these positions. (Real crossings between states of different symmetry do not contribute in an important way in the very low energy range.) In general, R_x is well reproduced by all methods which give the correct dissociation energies associated with the entry and exit channels. On the other hand, the determination of $\Delta E(R_x)$ is more delicate. The paucity of published data makes a quantitative comparison of the various methods difficult. However, some idea may be gained by a comparison of the model potential results (McCarroll and Valiron 1975, 1976, 1979, Gargaud et al. 1981, Opradolce et al. 1982) with the empirical formula proposed by Butler and Dalgarno (1980) on the basis of their configuration interaction results. They find that for type I processes, their results are reproduced to within 30% by the formula

$$\Delta E(R_x) = 27.2 \, R_x^2 \exp(-\beta R_x) \text{ eV} \tag{8}$$

where $\beta = 1$ in the case of neutral atomic hydrogen and $\beta = 1.34$ for neutral helium. For the systems listed in Table 1, there is good reason to believe that the model potential results should be accurate. In some cases there is satisfactory agreement between the different methods (N IV/H, B IV/He) but in other cases the discrepancy can sometimes be quite considerable. It is thus clear that an empirical formula, which makes no allowance for the particular symmetry of the final state is unsatisfactory.

COLLISION DYNAMICS

The absence of good experimental data at eV energies has necessitated extensive reference calculations in order to develop simpler models.

Table 1. Energy differences $\Delta E(R_x)$ at avoided Σ-Σ crossings of potential
energy curves in various systems.

$\Delta E(R_x)$ in eV

System	$R_x(a_o)$	Empirical formula (8)	Model potential
N IV/H	9.0	0.27	0.34
Si III/H	9.7	0.15	0.07
C V/H	7.9	0.60	0.10
	7.4	0.91	1.09
	7.1	1.19	2.01
B IV/He	4.5	1.32	1.99
	7.4	0.07	0.07
Ar VII/He	7.4	0.07	0.37
	5.8	0.39	1.33
	3.6	2.8	4.7

A detailed description of these calculations would be out of place in
this review but it is useful to recall the essential steps (Heil et al.
1981, Gargaud et al. 1981).

Basically, a complete description of the collision dynamics requires
not only the adiabatic energy curves but also the dynamic coupling matrix
elements (both radial and rotational) between the different adiabatic
states intervening in the collision. The calculation of these matrix ele-
ments is a delicate operation and approximations (often of uncertain
validity), such as the Hellmann-Feynman theorem are frequently used to
simplify the·calculations. This is the case for the calculations of
Butler (1981). Even when the matrix elements can be computed without
approximation, as in the model potential calculations, great care must
be exercised to avoid all possible errors. Once determined, these matrix
elements serve to define a diabatic transformation (Smith 1969) which
leads to a considerable simplification of the scattering equations.

The smooth variation of the elements of the diabatic potential mat-
rix in the vicinity of the avoided crossings, as compared with the dyna-
mic coupling matrix elements (see figures 2 and 3) would suggest the
possibility of their empirical construction directly from the adiabatic
potential curves.

This is, of course, the essence of the Landau-Zener (LZ) method,
which defines the diabatic transformation using the computed values of
$\Delta E(R_x)$ and assuming that the diagonal potential matrix vary linearly. An
approximate solution of the dynamical equations in the semi classical
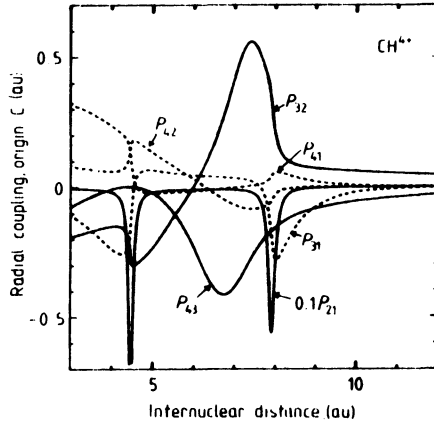
Fig. 2. Radial matrix elements for the Σ states of CH^{+4}. The full curves designate the principal coupling terms P_{21}, P_{32}, P_{43}. The broken curves refer to the less important coupling terms P_{31}, P_{41}, P_{42}.
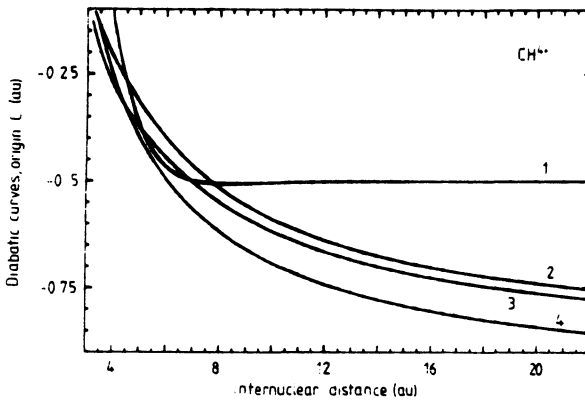

Fig. 3. Diagonal elements of the diabatic potential matrix of CH^{+4} constructed from the radial matrix elements of fig. 2 .

(impact parameter) treatment then yields a total cross section of the form

$$Q = 2\pi \int_0^{b_m} 2w(1-w) \; b \; db \qquad (9)$$

where b_m is the maximum value of impact parameter b, for which the crossing point R_x is classically accessible and

$$w = \exp\left[\{-\pi \; \Delta E(R_x)^2 \; R_x^2 \}/\{2(q-1)v\}\right] \qquad (10)$$

where v is the radial velocity at R_x. Typical applications of the LZ formula usually assume straight line trajectories, which is valid at energies exceeding a few eV. At thermal energies, it is more reasonable to assume b_m and v to be determined by the polarization potential of the entry channel. This modification enables the LZ approximation to take
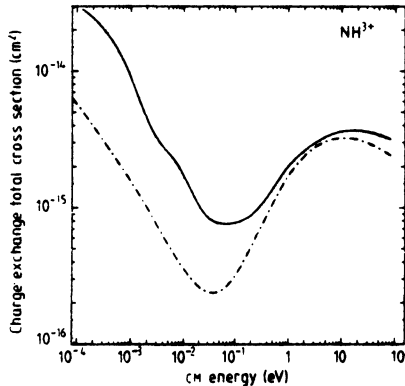
Fig. 4. Charge exchange cross section (in units of cm^2) in N IV/H colli-
sions as a function of energy (in eV). The full curve designates the
quantum mechanical calculations. The broken curve refers to the Landau-
Zener model with allowance for trajectory effects(Gargaud et al.).

account of orbiting effects, at least in a qualitative manner. The accu-
racy of the LZ formula can be satisfactory ($\sim$20-30%) when the values of
w, which contribute most to the integrated cross section Q are of the
order of 0.5. When w becomes very small (adiabatic limit) or approaches
1 (diabatic limit) the LZ formula becomes unreliable. A typical compari-
son with an exact calculation is given in figure 4 for charge exchange
in N IV/H collisions.

It is clear from the preceding paragraph that the LZ formula, alt-
hough very simple to use, is the result of a series of approximations,
whose validity is difficult to ascertain. In actual practice, most of
these approximations are unnecessary since there is no fundamental diffi-
culty in solving numerically the quantum mechanical scattering equations
once the diabatic potential matrix is known. The only really useful app-
roximation is the empirical construction of the diabatic potential mat-
rix from the adiabatic potentials without having recourse to the calcu-
lation of the radial matrix elements. This approach has been followed in
the work of McCarroll and Valiron (1976, 1979) for the Si III/H and N IV/
H systems, where various parametric forms of the diabatic matrix are
proposed. The success of the approach can be judged by a comparison with
the results of the exact calculations of Gargaud et al.(1981). More recent
calculations, currently in progress, based on a technique developed by
Masnou-Seeuws et al. (1982) in another context (see also Faist and Levine
1976), confirm the validity of an empirical construction of the diabatic
potential matrix and allow the determination of confidence limits of the
method in a given situation. Typical comparisons are shown in Table 2.

The excellent agreement between the exact and empirical diabatic
transformation confirms the feasibility of calculating cross sections on
the basis of good adiabatic potential curves alone, at least in the energy
range of astrophysical interest.

Table 2. Cross sections (in units of a_o^2) at a collision energy (c.m) of 0.8 eV

System	Exact radial coupling	Empirical diabatic matrix
C V/H	55	46
N IV/H	65	58
Si III/H	143	149

RESULTS AND DISCUSSION

     The essential problem is to know to what extent the theoretical cross sections can be relied upon. For type I processes, present indications are that the theory can produce results of high accuracy. There is a good consistency between the different theoretical approaches (configuration interaction, frozen core Hartree Fock, model potential) and there is excellent agreement between theory and experiment for those systems where comparison is possible. For example, (see fig. 5) the recent experimental results of Phaneuf (1981) on the system C V/H in the centre of mass energy range from 10 to 500 eV and of Huber (1982) on the system N IV/H in the energy range from 100 to 300 eV agree very satisfactorily with the theoretical results of Gargaud et al.(1981, 1982). Less well tested are the individual cross sections for capture into a specific excited state. These are more sensitive to details of the theoretical model and a real test of the theory must await more detailed experiments. For example, Dalgarno et al. (1981) do not guarantee even the largest capture cross sections for the system O IV/H to more than a factor of three.

     As for type II processes, there exists for the moment, only the theoretical data of Butler et. (1980) No comparison with experiment has yet been possible
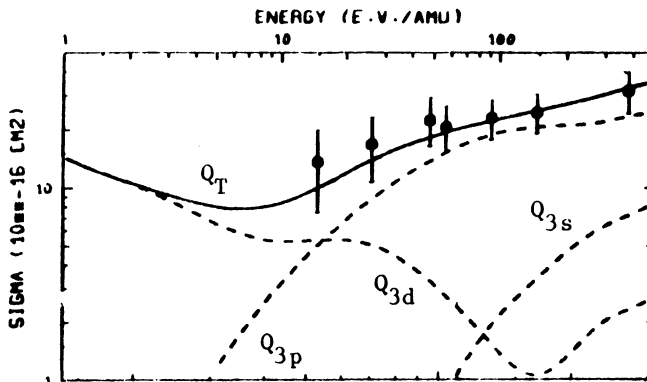

Fig. 5. Charge exchange cross sections in C V/H collisions as a function of the incident ion beam energy. The theoretical results of Gargaud et al. are compared with the experimental results of Phaneuf.

ACKNOWLEDGMENTS

REFERENCES

Baliunas, S.L. and Butler, S.E.: 1980, Astrophys. J. Letters 235, L45
Butler, S.E.: 1981, Phys. Rev. A23, 1
Butler, S.E. and Dalgarno, A.: 1980, Astrophys. J. 241, 838
Butler, S.E., Heil, T.G. and Dalgarno, A.: 1980, Astrophys. J. 241, 442
Christensen, R.B., Watson, W.D. and Blint, R.J.: 1977, Astrophys. J. 213,
     712
Dalgarno, A.: 1978, IAU Symposium N° 72 on Planetary Nebulae
Dalgarno, A., Butler, S.E. and Heil, T.G.: 1980, Astron. Astrophys. 89,
     379
Dalgarno, A., Heil, T.G. and Butler, S.E.:1981, Astrophys. J. 245, 793
Faist, M.B. and Levine, R.D.: 1976, J. Chem. Phys. 179, 111
Gargaud, M., Hanssen, J., McCarroll, R. and Valiron, P.: 1981, J. Phys. B:
     Atom. Molec. Phys. 14, 2259
Gargaud, M., Hanssen, J., McCarroll, R. and Valiron, P.: Physics of Elec-
     tron and Atomic Collisions, Invited Papers XII ICPEAC, (edited
     S. Datz), p. 707, North-Holland Amsterdam (1982)
Gargaud, M., Hanssen, J., McCarroll, R. and Valiron, P.: Communications
     au 2e colloque national du conseil français du télescope spatial,
     p. 77, INAG Paris (1982)
Gargaud, M., McCarroll, R. and Valiron, P.: 1982, Astron. Astrophys.
     106, 197
Heil, T.G., Butler, S.E. and Dalgarno, A.: 1981, Phys. Rev. A23, 1100
Huber, B.A.: 1982, Physica Scripta, Topical issue on Physics and Produc-
     tion of Highly Charged Ions, to appear
Janev, R.K.: 1982, Physica Scripta, Topical Issue on Physics and Produc-
     tion of·Highly Charged Ions, to appear
McCarroll, R. and Valiron, P.: 1975, Astron. Astrophys. 44, 465
McCarroll, R. and Valiron, P.: 1976, Astron. Astrophys. 53, 83
McCarroll, R. and Valiron, P.: 1979, Astron. Astrophys. 78, 177
McCarroll, R. and Valiron, P.: 1978, J. Physique 39, C1, 52
Masnou-Seeuws, F., Boulmer, J., Maurin, T., Roche, A.L. and Valiron, P.:
     1982, J. Phys. B: Atom. Molec. Phys., to appear
Ohtani, S.: 1982, Physica Scripta, Topical issue on Physics and Produc-
     tion of Highly Charged Ions, to appear
Opradolce, L., Valiron, P. and McCarroll, R.: 1982, J. Phys. B: Atom.
     Molec. Phys., to appear
Péquignot, D.: 1980 a, Astron. Astrophys. 81, 356
Péquignot, D.: 1980 b, Astron. Astrophys. 83, 52
Péquignot, D., Aldrovandi, S.M.V. and Stasinska, G.: 1978, Astron. Astro-
     phys. 63, 313
Phaneuf, R.A.: 1981, Phys. Rev. A24, 1138
Smith, F.T.: 1969, Phys. Rev. 179, 111
Ulrich, M.H. and Péquignot, D.: 1980, Astrophys. J. 238, 45
Watson, W.D. and Christensen, R.B.: 1979, Astrophys. J. 231, 627

TARTER: Does your comment on the lack of validity of the Butler–
Dalgarno prescription for ΔE apply to their general methodology or
just to the use of the simple formula?

McCARROLL: The limitation of the Butler–Dalgarno prescription for ΔE
applies only to the use of their simple formula. The value of ΔE is
determined not only by ionization potentials but also by the symmetry
properties of the molecular states involved. An empirical formula,
which takes no account of such symmetry, cannot predict the correct
values of ΔE. Of course, the configuration interaction calculations
of Butler are not, in principle, subject to such limitations.

SEATON: Charge transfer can also give rise to observable spectrum
lines: O III singlets are discussed by Dalgarno, Heil and Butler
(Astrophys. J., 245, 793) and triplets by Dalgarno and Sternberg
(Mon. Not. R. Astron. Soc., in press).

PEQUIGNOT: The importance of charge exchange as an ionizing process
should be emphasized. We found that the abundances of several minor
species are reduced by a factor of 10 when this process is introduced
in the recent model of NGC 7662 by Harrington et al. (see the review
of Harrington in this volume). Also, Si^+ is depleted by about a
factor of 3.

McCARROLL: I agree entirely. Some remarks on the selective nature of
ionization by charge exchange are given in the written version of
my talk.