Charge transfer and fine-structure transitions in
\( \text{Ar}^+ (^3\text{P}) + \text{Ar}(^1\text{S}) \) collisions

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Abstract. Cross sections for charge transfer and fine-structure transitions within the \(^3\text{P}\) multiplet have been calculated for the \( \text{Ar}^+ (^3\text{P}) + \text{Ar}(^1\text{S}) \) collision using the atomic eigenfunction expansions in the impact-parameter method and neglecting momentum transfer. Formulae for the exchange energies, valid at large inter-nuclear separations, were obtained for the \( \Sigma \) and \( \Pi \) states, and the spin–orbit effects were included as an energy defect. The six coupled equations, with and without rotational coupling, were solved numerically for those energies at which the velocity of the incident ion is comparable to the fine-structure splitting in atomic units, and the resulting transition probabilities were integrated approximately. It is found that the two fine-structure states \( j = \frac{1}{2} \), \( j = \frac{3}{2} \) undergo charge transfer with near-equal efficiency and have, to this order, the usual symmetric resonance behaviour. Further, the spin-change cross sections are significantly affected by the inclusion of rotational coupling.

1. Introduction

The importance of fine structure in charge-transfer collisions between rare-gas atoms and ions has been of recent experimental interest (cf. Hasted 1968). Gilbody and Hasted (1956) first suggested that in low-energy collisions the spin–orbit splitting of the \(^2\text{P}\) multiplet of the rare-gas ion might have a significant effect on the total charge-transfer cross section. Recent experimental evidence has not borne this out. In addition there have been discrepancies in experimental results on the relative efficiencies of the two processes

\[
\text{X}^+ (^3\text{P}_{3/2}) + \text{X} \rightarrow \text{X} + \text{X}^+ \\
\text{X}^+ (^3\text{P}_{1/2}) + \text{X} \rightarrow \text{X} + \text{X}^+.
\]

Theoretical work to date on these rare-gas ion–atom collisions has neglected the spin–orbit splitting and used a single exchange potential of the type used for \( \Sigma \) states to obtain estimates of the total charge-transfer cross section. In this paper the \( \Sigma \) and \( \Pi \) exchange splittings, resulting from the \(^2\text{P}\) multiplet of the ion, are estimated and fine-structure effects are included to lowest order. Consequently we hope to be able to determine the behaviour of the total charge-transfer cross section, the relative efficiencies of the processes in equation (1), and obtain first estimates of the cross sections for fine-structure transitions as functions of incident ion energy.

The energetically interesting region is that for which the magnitude of the velocity of relative motion is comparable to that of the spin–orbit splitting when both are expressed in atomic units. As the change in energy involved in a transition is small compared with the kinetic energy the impact-parameter approximation is employed. Further, the change in momentum of the captured electron, polarization effects, and coupling to higher states are neglected.

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The formulation of the problem is essentially that carried out by Nikitin (1965) for non-adiabatic fine-structure transitions in the collision of a $^1S_o$ atom with an alkali metal atom in a $^2P$ state and consequently we incorporate some of the notation used. Our problem differs from this in that the centres of nuclear charge are identical and we are considering symmetric charge transfer. However, replacing the potentials in the above reference by exchange potentials, the resulting differential equations will be similar in form to those in § 2. Atomic units are used throughout this work.

2. Description of the problem

Because the velocities are small the total wave function can be accurately expanded in terms of the ground-state $^2P$ multiplet functions. Writing for the total wave function

$$\Psi_{jm_1}(t) \simeq \sum_{j',m_2} \{a_{j'm_1}(t)|j', m_2; a\rangle + b_{j'm_1}(t)|j', m_2; b\rangle\}$$

one solves the equation

$$\left(\mathcal{H} - \frac{i}{\hbar} \frac{\partial}{\partial t}\right) \Psi_{jm_1}(t) = 0. \tag{3}$$

The labels $a, b$ in equation (2) refer to the two centres of nuclear charge. Therefore by $|j, m_2; a\rangle$ we represent the product of the atom–ion many-electron functions with the extra electron on centre $a$. The labels $j'$ and $m_1$ refer to the separated atom quantization and the subscripts on $\Psi(t)$ may refer to the initial conditions, e.g. $a_{jm_1}(\infty) = 1$, with the other coefficients zero as $t \to -\infty$.

The Hamiltonian $\mathcal{H}$ can be written in the form $\mathcal{H} = H_0 + W$ where $W$ is the spin–orbit interaction operator and $H_0$ is the Hamiltonian of the quasi-molecule $X_2^+$ depending on the inter-nuclear separation $R$. The relevant eigenstates of $H_0$ are labelled $^3\Sigma_{g,u}$ and $^3\Pi_{e,u}$. In the separated-atom limit these go to the $^3P$ states. In the one-electron approximation the states $|j, m_1\rangle$ are related to the states labelled $m_i, m_a$, the orbital and spin angular momentum quantum numbers, by

$$|\frac{3}{2}, \pm \frac{3}{2}\rangle = |\beta\rangle |^{3}\Sigma_{+1}\rangle$$

$$|\frac{3}{2}, \pm \frac{1}{2}\rangle = \sqrt{\frac{2}{3}} |\beta\rangle |^{3}\Sigma_{0}\rangle + \sqrt{\frac{1}{3}} |\gamma\rangle |^{3}\Pi_{1}\rangle$$

$$|\frac{1}{2}, \pm \frac{1}{2}\rangle = \pm \sqrt{\frac{1}{3}} |\beta\rangle |^{1}\Sigma_{0}\rangle \mp \sqrt{\frac{1}{3}} |\beta\rangle |^{1}\Pi_{0}\rangle$$

where the labels signify the projection of angular momentum along the $z$ axis and $\alpha$ and $\beta$ are the spin functions. The interaction operator $W$ is assumed to be independent of $R$ to lowest order, and the magnitude of the spin–orbit splitting is given by

$$^2P_{1/2}|H|^2P_{1/2} - ^2P_{3/2}|H|^2P_{3/2} = \Delta \varepsilon.$$  

We consider two approximations. In the first the $z$ axis, the axis of quantization, lies along $R$ (molecular model) and in the second the $z$ axis is fixed in space (atomic model); the latter includes directly the rotational coupling (cf. Bates and McC Carroll 1962). The matrix elements in the two models can be written in terms of the exchange energies

$$\Delta E_{12} \equiv \begin{cases} \frac{1}{2}(E_{1}^x - E_{2}^x) \\ \frac{1}{4}(E_{1}^y - E_{2}^y) \end{cases} \quad \Delta E_{11} \equiv \begin{cases} \frac{1}{2}(E_{1}^x + E_{1}^y) \end{cases}$$

and the spin–orbit splitting $\Delta \varepsilon$. There is a direct interaction of order $1/R^4$, but as it
is independent of state, neglecting 'higher-order' terms, it can be integrated out of the equation.

In the molecular model the resulting equations are (cf. Nikitin 1965):

\[
\frac{i}{\hbar} \frac{\partial}{\partial t} a_{3/2,3/2} \approx \Delta E_{41} b_{3/2,3/2} = (\vec{r} - \frac{1}{3}\Delta V) b_{3/2,3/2}
\]

\[
\frac{i}{\hbar} \frac{\partial}{\partial t} a_{3/2,1/2} \approx (\vec{r} + \frac{1}{3}\Delta V) b_{3/2,1/2} + \frac{\sqrt{2}}{3} \Delta V b_{1/2,1/2} \exp(-i\omega t)
\]

\[
\frac{i}{\hbar} \frac{\partial}{\partial t} a_{1/2,1/2} \approx \vec{r} \cdot b_{1/2,1/2} + \frac{\sqrt{2}}{3} \Delta V b_{3/2,1/2} \exp(i\omega t)
\]

(5)

together with a corresponding set coupled to this in which the \(a\)'s and \(b\)'s are interchanged. In equations (5) the rotation of the internuclear axis and terms of the order of the square of the overlap,

\[S_{jm} = |\langle j, m_j| a| j, m_j| b \rangle|^2
\]

have been neglected. Further

\[\vec{r} = \frac{1}{6}(\Delta E_{22} + 2\Delta E_{11}), \quad \Delta V = (\Delta E_{22} - \Delta E_{11})\]

and \(\omega = \Delta \epsilon\) in atomic units. Equations (5) can be solved analytically when the relative velocity is large (cf. § 5).

The most convenient choice of \(z\) axis in the atomic model is that perpendicular to the collision plane. From figure 1 the new atomic states \(\overline{|jm_j\rangle}\) can be obtained by a rotation from the states quantized along \(R\), that is,

\[\overline{|jm_j\rangle} = \exp(i\gamma J_{z'}) \exp(-i\frac{\pi}{2} J_{\phi})|jm_j\rangle\]

(6)

where \(J_{z'}\) and \(J_{\phi}\) are the angular-momentum operators associated with the \(z'\) and \(\phi\) axes and \(\gamma\) is the angle of rotation of the molecular axis. The matrices associated with these operators are particularly simple (cf. Messiah 1962). The equations in the

![Figure 1. Coordinate systems: full lines, molecular model; broken lines, atomic model. The positions of the nuclei are labelled \(a\) and \(b\), and \(\vec{r}\) is the direction of the velocity of the incident ion.](image-url)
space-fixed axes are now

\[
i \frac{\partial}{\partial t} \tilde{a}_{3/2,-3/2} \simeq \left( \Gamma + \frac{1}{6} \Delta V \right) \tilde{b}_{3/2,-3/2} - \frac{1}{2\sqrt{3}} \Delta V \tilde{b}_{3/2,2/2} \exp(2iv\eta) \\
+ \frac{1}{\sqrt{6}} \Delta V \tilde{b}_{1/2,1/2} \exp(-i\omega t + 2iv\eta) \]

\[
i \frac{\partial}{\partial t} \tilde{a}_{3/2,1/2} \simeq \left( \Gamma + \frac{1}{6} \Delta V \right) \tilde{b}_{3/2,1/2} + \frac{1}{2\sqrt{3}} \Delta V \tilde{b}_{3/2,-3/2} \exp(-2iv\eta) \\
- \frac{1}{3\sqrt{2}} \Delta V \tilde{b}_{1/2,1/2} \exp(-i\omega t) \]

\[
i \frac{\partial}{\partial t} \tilde{a}_{1/2,1/2} \simeq \Gamma \tilde{b}_{1/2,1/2} + \frac{1}{\sqrt{6}} \Delta V \tilde{b}_{3/2,-3/2} \exp(i\omega t - 2iv\eta) \\
- \frac{1}{3\sqrt{2}} \Delta V \tilde{b}_{3/2,1/2} \exp(i\omega t) \]  

(7)

In transforming from the atomic to the molecular model terms of the order \((\Gamma/\Delta V)\) are dropped. Consequently the set of equations (5) is accurate only in the region where \((\Gamma/\Delta V) \ll 1\).

The symmetry of the problem could be used to separate both equations (5) and equations (7) into two sets of three coupled equations. In the final analysis we are interested in determining the coefficients \(a \) and \(b \) so computationally nothing would be gained. It should be noted that the coupling potentials are in all cases proportional to \(\Delta V\), the difference between the \(\Sigma\) and \(\Pi\) exchange energies.

3. The exchange potentials

The exchange potentials can be estimated quite simply by using a one-electron Coulomb wave function at those inter-nuclear separations for which the overlap, \(S_{\text{int}}\), is small (cf. Smirnov 1965). In this region the ionization potential determines the behaviour of the atomic wave function (Bates and Damgaard 1949) and as the rare-gas atoms are closed-shell systems the one-electron approximation should be sufficiently accurate.

This method, first suggested by Firsov (1951), is by now familiar. Neglecting spin, the exchange energies are calculated from surface integrals of the form (cf. Smirnov 1965),

\[
\Delta E_i \simeq -\frac{1}{2} (1 - \mathcal{P}) I \int_0^\infty d\sigma \left[ \hat{q}_i(1_a) \hat{q}_i(1_b) - \hat{q}_i(1_a) \hat{q}_i(1_b) \right] z_0 
\]

where \(\varphi_i\) is the perturbed Hartree-Fock spatial orbital of the active electron; \(1_a\) and \(1_b\) are the distances of the electron from the centres \(a\) and \(b\); \(z\) is measured along the axis connecting \(b\) to \(a\); \(\mathcal{P}\) is determined by the behaviour of the atomic functions under inversion; \(I\) is a correction factor, which is a measure of the difference of the orbitals on the ion from those on the atom. In equation (8) the integral is carried out over the plane bisecting the inter-nuclear axis and perpendicular to it; for \(Ar_2^+\), \(\mathcal{P} = 0\) and \(I \approx 0.98\), which indicates that the Hartree-Fock corrections are the...

\[\text{†}\] For the molecular model—in effect two coupled equations. The differential equations for \(a_{3/2,2/2}\) and \(b_{1/2,1/2}\) are exactly soluble.

\[\text{‡}\] The value of \(I\) was obtained from analytic Hartree-Fock orbital functions (Clementi 1965); \(I \approx \hat{\Pi \cdot \hat{\Pi}}\). \(\varphi_i\) represent the orbitals on the ion and atom respectively.
order of a few per cent for large $R$.

Writing $\varphi_m(1) \approx \phi_p(r_1) Y_1^{m_1}(\Omega_1)$, where the $Y_1^{m_1}$ are the spherical harmonics, then the $\Sigma$, $\Pi$ exchange energies become

$$\Delta E_{\Sigma11} \simeq -\frac{1}{2} \left(\frac{3R}{4}\right) \int_{R/2}^{\infty} \phi_p^2(r) \frac{dr}{r}$$

and

$$\Delta E_{\Pi11} \simeq -\frac{1}{2} \left(\frac{3R}{4}\right) \phi_p\left(\frac{R}{2}\right) + \Delta E_{11}$$

where $R$ is the internuclear distance. For large $R$, the perturbed radial wave function, to lowest order, is

$$\phi_p(r) \simeq \left(\frac{4}{\pi}\right)^{1/2} \phi_p^{\text{atomic}}(r)$$

(cf. Smirnov 1965), where $\phi_p^{\text{atomic}}(r)$ is obtained from the Coulomb approximation and $n = (2E)^{-1/3}$, where $E$ is the ionization potential of the atom. In the above formula only the lead term in a $1/R$ expansion is accurate. Therefore, the general form for the exchange energies becomes

$$\Delta E_{\Sigma} \simeq A \left(\frac{R}{n}\right)^{2n-1} e^{-R/n}$$

and

$$\Delta E_{\Pi} \simeq -\left(\frac{n}{R}\right) \Delta E_{\Sigma}$$

where

$$A = \frac{3}{4} \left(\frac{4}{\pi}\right)^{1/2} \left(\frac{n}{2}\right)^{2n-1} \frac{1}{N}$$

and where $N$ is the normalization constant of the Coulomb function. As $n$ is small, e.g. $n = 0.929$ for argon, $N$ is best estimated by fitting the Coulomb function to the tail of the appropriate Hartree–Fock orbital at as small a radial distance as possible. For argon, using an analytic orbital function (Clementi 1965), $N^{-1/3} \approx 2.02$ and depends slightly on the point at which the two functions are joined.

The expression for the $\Pi$ potential was tested on $\Pi(2p^1)+\Pi^+$ and compared with the results of Bates and Reid (1968). The differences between the estimated and accurate values were less than 20% of the accurate value for inter-nuclear distances $R/n \gtrsim 3$. Because the rare-gas $2p^1$ ground states are tightly bound, the perturbation effect due to mixing in of higher states will be less important and the accuracy might be even better in the region where the one-electron approximation applies, i.e. when $S_m \ll 1$.

Approximate adiabatic exchange potentials, using the basis set of equation (2) to diagonalize $H$, are displayed in figure 2 for $Ar^+\Pi$ where the spin-orbit splitting as $R \to \infty$ is $\Delta \epsilon = 0.00653$ a.u. The potentials can be divided into three regions: region III where the exchange energies dominate, $(\Lambda, S)$ coupling; a ‘non-adiabatic’ region defined by a distance $R_1$, $\Delta V(R_1) = \Delta \epsilon$, and of extent $\delta R \sim n$, where the breakdown of the spin orbit coupling occurs: $R_1 = 7.2$ a.u. for $Ar^+_2$; finally for very large $R$ where the spin–orbit interaction dominates, $(J_\sigma,J_\alpha)$ coupling (cf. Herzberg 1950).

### 4. Calculations

The set of coupled differential equations (5) for the molecular model was integrated for a number of impact parameters to obtain probabilities for charge transfer and spin
change without rotational coupling. The effect of the rotation of the inter-nuclear axis on these probabilities was found by a similar integration of the set (7) for the atomic model. These integrations were carried out by a Runge–Kutta method employing two step sizes, the first used in potential regions I and II, figure (2), and the other in region III, where the exchange energies become large. Because the rotational coupling was included via the atomic model, rather than adding terms of the order $1/R^2$ to the molecular model, and the potentials decay exponentially, the range of integration can be kept relatively small in all cases.

![Diagram of exchange energies](image)

Figure 2. The exchange energies for $A_2^+$ in units of the spin–orbit splitting as a function of inter-nuclear separation $R$, in atomic units. For this system $\Delta_r = 0.0065$ a.u., the spin–orbit splitting, and $\alpha = 0.929$, the atomic Coulomb quantum number. The non-adiabatic region, region II, is indicated approximately by the broken lines. In region I ($J_a, J_c$) coupling dominates, and in region III ($A, S$) coupling.

Cross sections, with and without rotational coupling, were computed from these probabilities, which oscillated irregularly (figure 3), by dividing the range of impact parameters, $p_1 < p_2 < p_3$. In the region $p_1$ to $p_2$ the oscillations were rapid and average probabilities $\bar{P}$ were obtained. These were used to estimate the contributions of the cross sections from the region $(0, p_2)$, i.e. $\sigma \approx \pi(p_2)^2\bar{P}$. Simpson’s rule was used from $p_2$ to $p_3$, and a Gauss-Laguerre quadrature from $p_3$ to \( \infty \). The average time to obtain a set of cross sections from equations (7) was about 500 s on an ICT 1907 computer. The calculated average probabilities, plotted as a function of energy, were adjusted to fit a smooth curve. For the non-adiabatic transitions the behaviour
of the average probabilities agreed closely with that predicted by the formula of Rosen and Zener (1932),

\[
\left| \int_{-\infty}^{\infty} \frac{\Delta V \exp(-i\omega t) dt}{\int_{-\infty}^{\infty} \Delta V dt} \right|
\]
evaluated at zero impact parameter, where \( \Delta V \) is the coupling potential.

The greatest uncertainty in the calculation of the cross sections is due to the potentials, equations (9) and (10). An error in the constant \( A \) would correspond to

![Figure 3. The probability of change transfer with fine-structure transition \( j = \frac{1}{2} \rightarrow j = \frac{1}{2} \) (\( \text{Ar}^+ \rightarrow \text{Ar} + \text{Ar}^\alpha \)) at incident ion energy \( \Delta = 400 \text{ ev} \), and with \( \Delta \epsilon \Delta V = 0.32 \text{ A.U.} \), obtained by numerical integration of equations (7).]

a shift of the cross sections in energy, whereas the absence of the higher-order terms in \( 1/R \) cause the cross sections at higher energies to be uncertain by a factor \( 1 \pm O(1/e) \). If the overall uncertainty in the potentials were \( 20^{\circ} \), for the important inter-nuclear distances this could be manifested by a shift in the results on the \( \ln \sigma \) scale by \( \pm 0.2 \) or by an uncertainty in the magnitude of the total charge-transfer cross section of about \( 8^{\circ} \), and for the transition cross sections almost twice this at high energies. For smaller energies the high-order terms affect the transitions via the coupling \( \Delta V \). By adding terms to \( \Delta E_\alpha \) of higher-order in \( 1/R \) we estimate that the magnitudes of the transition cross sections in the vicinity of the maxima have an uncertainty of about \( 20^{\circ} \), in addition to the possibility of being shifted as above.

\( \dagger \) The momentum transfer begins to be a factor here also (cf. Bates and McCarroll 1962).

\( \ddagger \) This should not be taken as a measure of the effect of \( \Delta E_{11} \) on these cross sections. Setting \( \Delta E_{11} \) to zero changes these results by as much as \( 50^{\circ} \) in this region.
5. Firsov cross sections

For velocities large compared with the spin orbit splitting, the inter-nuclear separations of importance are those in region III where the spin-orbit splitting can be neglected and the $\Sigma$, $\Pi$ states diagonalize $\mathcal{H}$. The interaction is assumed to be spin-independent and the sets of equations (5) and (7) can be replaced by those in the $m_l$ representation

$$\frac{d}{dt} a_{\pm\lambda} \simeq \Delta E_{\pm\lambda} \hat{b}_{\pm\lambda}$$

and

$$\frac{d}{dt} \tilde{a}_{\pm\lambda} \simeq \Delta E_{\pm\lambda} \tilde{b}_{\pm\lambda}$$

where the subscripts imply the projection of orbital angular momentum along the axis of quantization and $\mathcal{E} = \frac{1}{2} (\Delta E_{\Sigma} + \Delta E_{\Pi})$.

The set of equations (5') is easily solved as it has the form of the symmetric resonance charge transfer problem (cf. Bates and McCarroll 1962). Writing

$$\zeta_{\Sigma} \equiv \frac{1}{\tau} \int_{-\zeta}^{\zeta} \Delta E_{\Sigma} \, dz$$

and

$$\zeta_{\Pi} \equiv \frac{1}{\tau} \int_{-\zeta}^{\zeta} \Delta E_{\Pi} \, dz$$

the probabilities of charge transfer can be calculated using the vector coupling coefficients in equation (4) as weights. The total charge-transfer probability is independent of the initial $j$ state in this region (cf. Appendix):

$$P_{\Sigma}^{\text{CT}} = \frac{2}{3} P_{\Pi}^{\text{CT}} + \frac{1}{3} P_{\Sigma}^{\text{CT}}$$

where $P_{\Sigma}^{\text{CT}} = \sin^2 \zeta_{\Sigma}$ and $P_{\Pi}^{\text{CT}} = \sin^2 \zeta_{\Pi}$. The probability of charge transfer with spin change if the initial state is $j = \frac{3}{2}$ is

$$P_{\Sigma, \Pi, \frac{3}{2}, \frac{1}{2}}^{\text{CT}} = \frac{1}{2} (\sin \zeta_{\Pi} - \sin \zeta_{\Sigma})^2$$

$$- \frac{1}{3} (P_{\Sigma}^{\text{CT}} + P_{\Pi}^{\text{CT}} + 2P_{(\Sigma - \Pi)/2}^{\text{CT}} - 2P_{(\Sigma + \Pi)/2}^{\text{CT}})$$

where

$$P_{(\Sigma + \Pi)/2}^{\text{CT}} = \sin^2 \{\frac{1}{2} (\zeta_{\Sigma} + \zeta_{\Pi})\} = \sin^2 \zeta_{(\Sigma + \Pi)/2}$$

The corresponding result for initial state $j = \frac{1}{2}$ is twice this. Similarly the probabilities of a fine-structure transition without charge transfer are

$$P_{\pm \frac{1}{2}, \pm \frac{1}{2}} = \frac{1}{4} (\cos \zeta_{\Pi} - \cos \zeta_{\Sigma})^2$$

$$= \frac{4}{3} P_{(\Sigma - \Pi)/2}^{\text{CT}} - P_{(\Sigma + \Pi)/2}^{\text{CT}}$$

$$= \frac{2}{3} [P_{(\Sigma + \Pi)/2}^{\text{CT}} + P_{(\Sigma - \Pi)/2}^{\text{CT}} - 2(P_{\Sigma}^{\text{CT}} + P_{\Pi}^{\text{CT}} - \sin^4 (\frac{1}{2} \zeta_{\Sigma}) - \sin^4 (\frac{1}{2} \zeta_{\Pi}))]$$

and again twice this for the $\frac{1}{2} \rightarrow \frac{3}{2}$ transition.
These probabilities can be integrated to obtain cross sections. A simple, accurate, well-known method for estimating these cross sections (cf. Bates and Boyd 1962) is that suggested by Firsov (1951). One writes

$$\sigma_i = 2\pi \int_0^\infty \rho \, d\rho \, \sin^2 \zeta_i(\rho) \approx \frac{1}{2} \pi \rho_0^2$$

where $\rho_0^2$ is the impact parameter which satisfies $\zeta_i(\rho_0^2) = 1/\pi$\dagger. The second, more complicated, expression in equation (13) behaves correctly at large velocity when integrated in this manner.

In the set of equations (7), which include rotational coupling, the solutions for $\tilde{a}_0$, $\tilde{b}_0$ are again obtained using the symmetric resonance charge transfer ones. Because of the angular dependence $\varphi$ in the differential equations for $\tilde{a}_{\pm 1}$, $\tilde{b}_{\pm 1}$, we use an approximation (cf. Nikitin 1965) obtained by the substitutions

$$a_{\pm 1} \rightarrow a_{\pm 1} \exp(\pm i\varphi) \quad b_{\pm 1} \rightarrow b_{\pm 1} \exp(\pm i\varphi)$$

and neglecting terms of the form $(i\hbar/t)\varphi \sim O(\hbar/R^2)$ in the region where the splitting $\Delta V$ dominates. The integration of the coupled equations can be started at that point in time when the inter-nuclear separation is $R_D$, defined by

$$\frac{\Delta V(R_D)}{\tau} \sim \delta$$

where $\delta$ is some small number, without significant loss in accuracy. The cross sections would then be obtained by integrating over impact parameters $0 < \rho < R_D$. We chose $R_D$ equal to the Firsov impact parameter for $\zeta_{\Sigma - \Pi}(0)$.

In this approximation the probability of charge transfer is identical to that in equation (11) and the changes in the transition probabilities due to rotational coupling are given by

$$\delta P_{3/2 \rightarrow 1/2}(\Delta \varphi) \simeq \frac{1}{2} (P_{11}^{\text{CT}} + P_{11}^{\text{CT}} - 2P_{11}^{\text{CT}}) \sin^2 \left( \frac{\Delta \varphi}{2} \right)$$

and

$$\delta P_{1/2 \rightarrow 3/2}(\Delta \varphi) \simeq \frac{1}{2} (1 - 2P_{11}^{\text{CT}} - 2P_{11}^{\text{CT}} + 2P_{11}^{\text{CT}}) \sin^2 \left( \frac{\Delta \varphi}{2} \right)$$

where $\Delta \varphi$ is the angle through which the molecular axis rotates during the integration and

$$\sin^2 \Delta \varphi = 1 - \left( \frac{\rho}{R_D} \right)^2.$$ 

These results give correctly the average probabilities as $\rho \rightarrow 0$ but are least accurate for large values of impact parameters, precisely those impact parameters of importance in the Firsov integration method.

The cross sections obtained from equation (11) by the Firsov method are in close agreement with the calculated total charge-transfer cross sections.\dagger For the non-adiabatic transitions the Firsov result is accurate only for charge transfer without rotational coupling. However, as seen in figure (5), the general behaviour and relative magnitudes are given correctly for the other cases.

\dagger For $\sin^2 \zeta_i$, in equation (13) the approximation

$$\int_0^\infty \rho \, d\rho \, \sin^2 \zeta_i \sim \frac{1}{2} \int_0^\infty \rho \, d\rho \, \sin^2 \zeta_i$$

is used and yields a result slightly larger than an accurate estimate.

\dagger The result which includes the rotational coupling is in fact about 4% larger at high energies.
When the velocity, in atomic units, is much less than the fine-structure splitting, the probability of transitions vanishes. The charge-transfer cross sections now depend on the initial $j$ state and are determined by the potentials in region I. From equations (5), one finds
\begin{equation}
P_{3/2}^{CT} \simeq \frac{1}{2} \sin^2 \xi_{11} + \frac{1}{2} \sin^2 \left( \frac{1}{3} \xi_{11} + 2 \xi_{1} \right)
\end{equation}
and
\begin{equation}
P_{1/2}^{CT} \simeq \sin^2 \left( \frac{1}{3} \xi_{1} + 2 \xi_{11} \right).
\end{equation}
Cross sections obtained from equations (16) and (17) are near equal in the region $\Delta\epsilon/c > 1$ a.u. and only begin to differ significantly for incident ion energies $E \lesssim 5$ ev. In addition, they are in close agreement with the cross sections obtained from the numerical integration.

6. Discussion

The calculated total charge-transfer cross section is in reasonable agreement with experimental results (figure 4).† Fine-structure effects of the type suggested by

![Spin-orbit splitting/velocity (A.U.)](image)

Figure 4. Total charge-transfer cross sections against incident ion energy $E$.


Gilbody and Hasted (1956) are not found and the cross section has, essentially, a symmetric resonance behaviour. The calculated ratio of the charge-transfer cross sections $\sigma(j = \frac{1}{2})/\sigma(j = \frac{3}{2})$, associated with the processes in equation (1), is not as sensitive to the approximations made here as the individual cross sections are. We

† For the other theoretical result in figure 4, Rapp and Francis (1962) use only a $\Sigma$ potential with a smaller interaction constant $A$ and a different criterion for choosing $\rho^*$ in the approximate integration of the charge-transfer probability.
obtain a value of unity for this ratio, with an estimated uncertainty of 5% for the energies considered. This agrees with the results of Davies and Gilbody (1969) and Amme and Haugsjaa (1968) for similar systems, whereas Hussain and Kerwin (1966) obtain a factor 1.3 for Ar+ + Ar at 1 keV. The cross sections for transitions are relatively large; for initial state $j = \frac{3}{2}$, twice the values in figure 5. Consequently, the above results for the total charge-transfer cross sections are explained, as the weights for the $\Sigma$ and $\Pi$ states are independent of the initial $j$ state (cf. Appendix) and the exchange energies, at large $R$, have the same dominant exponential behaviour independent of the state.

The inclusion of rotational coupling has only a small effect on the total charge-transfer cross section at large velocities. As this coupling provides an additional channel for the transitions, these cross sections (figure 5) are changed significantly over the full energy range when the rotational coupling terms are included. At high energies the transition cross sections also have an essentially symmetric resonance behaviour. Below that energy at which the Fissov impact parameter, associated with the smallest exchange splitting, $\Delta E_{11}$, becomes equivalent in magnitude to the internuclear separations in region II, roughly 600 ev, these cross sections have a completely non-adiabatic behaviour.

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Appendix

The total charge-transfer probabilities within a fine-structure multiplet are independent of the initial $J$ state for velocities such that $\Delta v/\langle v \rangle \ll 1$ a.u., where $\Delta v$ is a measure of the fine-structure splittings. First neglecting rotational coupling, one writes, to lowest order, the total charge transfer probability from a given state $(J, M_J)$,

$$P_{J M_J}^{CT} = \sum_{M_L, M_s} |a_{LSM_L M_s}^{JM_J}(\infty)|^2 = \sum_{M_L, M_s} \sin^2 \theta_{LSM_L M_s} |a_{LSM_L M_s}^{JM_J}(- \infty)|^2 \quad (A1)$$

where the labelling is obvious. The exchange energies are independent of the spin projection to lowest order, and the total charge transfer probability from a given $J$ state is

$$P_J^{CT} = \frac{1}{2J+1} \sum_{M_J} P_{J M_J}^{CT}.$$

Noting that the coefficients $a_{LSM_L M_s}^{JM_J}(- \infty)$ would equal the vector-coupling coefficient $\langle L_SL_M \mid M_s \mid JM_J \rangle$, one has

$$P_J^{CT} = \frac{1}{2J+1} \sum_{M_s} \left[ \frac{1}{2L+1} \sum_{M_L} \sin^2 \theta_{LSM_L M_s} \sum_{M_J} \langle LSLM_s \mid JM_J \rangle \right]^2.$$

By the sum rules (cf. Messiah 1962), we can now write

$$P_J^{CT} = \frac{1}{2L+1} \sum_{M_s} \sin^2 \theta_{LSM_L M_s},$$

which is independent of $J$ state. If rotational coupling is added in the manner suggested in the text (§5), that is, the rotated coefficients obtain an additional phase factor, then one has in the same way

$$P_J^{CT} = \frac{1}{2J+1} \sum_{M_L, M_s, M_s} \left| \tilde{h}_{LSM_L M_s}^{JM_J}(\infty) \right|^2$$

$$\approx \frac{1}{2J+1} \sum_{M_L, M_s, M_s} \left[ \sum_{M_J} \tilde{A}_{JM_L M_s}^{(L)} \exp(iM_L \Delta \varphi) \sin \theta_{LSM_L M_s} \langle LSLM_s \mid JM_J \rangle \right]^2$$

where the $\tilde{A}_{JM_L M_s}^{(L)}$ represents the constant rotation matrix in equation (6) and $\Delta \varphi$ is the change in the angle between the fixed axis and the molecular axis during the integration. This again reduces to the results in equation (A1).

For values of velocity, in atomic units, much less than the spin–orbit splitting, the charge transfer probabilities are not independent of $J$. If the spin–orbit splitting is small, the exchange energies associated with the different states will have the same exponential behaviour as determined by the ionization potential (see equations (9) and (10)). Consequently, the ratio of the cross sections between any two levels will be $1 \pm O(1/\langle v \rangle^2)$.

The above results depend on the validity of the approximations made in the text.

References


