Alkali-metal–halogen charge-exchange collisions

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An approximate quasiclassical treatment is presented for calculating the cross sections for charge transfer from a neutral alkali-metal atom colliding with a halogen atom (chlorine or fluorine). The electron is treated by the time-dependent perturbation in the two-state approximation. The two states are the ground (or the first-excited) state of alkali-metal atom and the ground state of the halogen negative ion. Charge-transfer cross sections are calculated as a function of relative velocity (v) of collision between $v = 0.01$ and 5 a.u. Qualitative features of these cross sections are compared with an earlier work on alkali-metal–oxygen collisions. An asymptotic formula at low velocities of collision ($v \to 0$) is obtained, which compares with the earlier formula obtained by Bates. At higher velocities cross sections are found to vary as $1/v^2$, as in the Born approximation.

I. INTRODUCTION

In a previous paper[1] (to be referred to as I), an approximate method was proposed for calculating the cross sections for single-electron excitation and transfer from a neutral alkali-metal atom colliding with atomic oxygen. In the present paper we obtain the charge-transfer cross sections of I for neutral atom-atom collisions in a rather straightforward manner by solving coupled differential equations in two-state approximations. We also obtain an asymptotic formula for the single-electron charge transfer at low collision velocities. This formula gives a similar asymptotic behavior with velocity and energy defect as the one obtained by Bates.[2] The formalism developed here is applied to find charge-exchange cross sections for a neutral alkali-metal atom, which initially is in its ground or first-excited state (represented by A or A^*), colliding with a halogen atom (represented by B). The reactions treated are

$$A + B \to A^+ + B^-,$$

$$A^* + B \to A^+ + B^-,$$
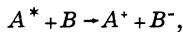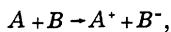
where A^+ and B^- are the ground states of the products. We assume straight-line classical trajectories for the colliding atoms and employ atomic units throughout.

II. THEORY

As is well known, collisions accompanied by charge exchange can be described over a wide energy range in a quasiclassical approximation in which the coordinates of the nuclei of the colliding atoms are stipulated time functions rather than dynamic variables. Under these conditions, the problem of charge exchange in the two-state approximation reduces to the problem of solving a pair of differential equations for the probability amplitudes of the states occupied by the electron before and after the collision. The two equations are obtained by expanding the total wave function of the system in terms of the initial and final states (i and j) of the electron and then using the time-dependent perturbation theory[1]:

$$i\dot{a}_i = [1/(1 - |S_{ji}|^2)][(V_{ii}^B - S_{ij}V_{ji}^B)a_i + (V_{ij}^A - S_{ij}V_{jj}^A)e^{-i\omega_{ji}t}b_j], \quad (1)$$

$$i\dot{b}_j = [1/(1 - |S_{ji}|^2)][(V_{ji}^B - S_{ji}V_{ii}^B)a_i e^{i\omega_{ji}t} + (V_{jj}^A - S_{ji}V_{ij}^A)b_j]. \quad (2)$$

We recall that, in deriving these equations, the Hamiltonian H describing the electron can be written

$$H = H_A + V^B = H_B + V^A,$$

where H_A or H_B is the unperturbed Hamiltonian when B or A^+ is not present. The unperturbed electron states are represented by ψ_i and φ_j, which are eigenfunctions of H_A and H_B, respectively, with energies ϵ_i^A and ϵ_j^B. All terms occurring in Eqs. (1) and (2) have the same meaning as in I, e.g.,

$$\omega_{ji} = \epsilon_j^B - \epsilon_i^A, \quad V_{ij}^A = \langle \psi_i | V^A | \varphi_j \rangle, \quad S_{ij} = \langle \psi_i | \varphi_j \rangle, \quad \text{etc.}$$

The coefficients a_i and b_j give, as functions of time, the admixture of states ψ_i and φ_j, the transition probability being proportional to $|b(\infty)|^2$.

Since ψ_i and φ_j belong to two different Hamiltonians, the above system of equations is non-Hermitian. The transformations given in I make the above system Hermitian. The general equations in the two-state approximation become[1]

$$i\dot{a} = Vb \exp\left(-i \int_0^t \alpha \, dt'\right), \tag{3}$$

$$i\dot{b} = Va \exp\left(+i \int_0^t \alpha \, dt'\right), \tag{4}$$

where

$$\alpha = \tilde{V}_{jj} - \tilde{V}_{ii} + \omega_{ji},$$

$$\tilde{V}_{jj} = V_{jj}^A,$$

$$\tilde{V}_{ii} = (V_{ii}^B - S_{ij}V_{ji}^B - S_{ji}V_{ij}^A)/(1 - |S_{ji}|^2),$$

$$V = |\tilde{V}_{ij}| = |(V_{ij}^A - S_{ij}V_{jj}^A)/(1 - |S_{ji}|^2)^{1/2}|.$$

We neglect the small time variation in the phase of the matrix element $\tilde{V}_{ij}$ compared with that obtained from the integrals in the exponents of Eqs. (3) and (4). This system of equations is then identical with Eqs. (3.3) and (3.4) in I.

Departing from the procedure used in I, we write the solution to Eqs. (3) and (4) in the form

$$a = A(t) \exp\left(-i \int_0^t \omega \, dt'\right), \tag{5}$$

$$b = B(t) \exp\left(-i \int_0^t (\omega - \alpha) \, dt'\right), \tag{6}$$

where $A(t)$, $B(t)$, and ω are real. Equations (3) and (4) then imply that

$$i\dot{A} = VB - \omega A, \tag{7}$$

$$i\dot{B} = VA - (\omega - \alpha)B. \tag{8}$$

Comparison of real and imaginary parts gives

$$\dot{A} = \dot{B} = 0$$

and

$$\omega_\pm = \tfrac{1}{2}\alpha \pm \delta,$$

where

$$\delta = \tfrac{1}{2}(\alpha^2 + 4V^2)^{1/2}.$$

The general solution to Eqs. (3) and (4) can thus be written

$$a(t) = A_1 \exp\left(-i \int_0^t \omega_+ \, dt'\right)$$
$$+ A_2 \exp\left(-i \int_0^t \omega_- \, dt'\right),$$

$$b(t) = B_1 \exp\left(-i \int_0^t (\omega_+ - \alpha) \, dt'\right)$$
$$+ B_2 \exp\left(-i \int_0^t (\omega_- - \alpha) \, dt'\right),$$

where A_1, A_2, B_1, and B_2 are constants. At large separations of the colliding atoms, $V \sim 0$, $\delta \sim \tfrac{1}{2}\alpha$, $\omega_+ \sim \alpha$, and $\omega_- \sim 0$. Therefore, we choose $A_1 = B_2 = 0$ and write the solution in the form

$$a = A \exp\left(i \int_0^t (-\tfrac{1}{2}\alpha + \delta) \, dt'\right), \tag{9}$$

$$b = B \exp\left(i \int_0^t (\tfrac{1}{2}\alpha - \delta) \, dt'\right), \tag{10}$$

where A and B are constants. This solution has the same form as that obtained in I, but is not based on the assumption of dropping terms of the form V'/V, α'/α, V''/V, etc., where the primes denote differentiation with respect to time.

We next obtain the transition probability from Eqs. (9) and (10) in a different manner from I. Dividing (10) by (9) and introducing a phase factor of $-\tfrac{1}{2}\pi$ in analogy to I and then differentiating with respect to time, we obtain

$$\frac{\dot{b}}{a} - \frac{b}{a^2}\dot{a} = -i[\dot{\mu} + i\mu(\alpha - 2\delta)] \exp\left(i \int_0^t (\alpha - 2\delta)dt'\right), \tag{11}$$

where

$$\mu(t) = \frac{B(t)}{A(t)} = \frac{|b(t)|}{|a(t)|}.$$

Using Eqs. (3), (4), (9), and (10), we obtain

$$V\left[(1 + \mu^2) \cos\left(\int_0^t 2\delta dt'\right)\right]$$
$$+ iV\left[(1 - \mu^2) \sin\left(\int_0^t 2\delta dt'\right)\right] = \dot{\mu} + i\mu(\alpha - 2\delta). \tag{12}$$

Comparing the real parts in Eq. (12), we have

$$\dot{\mu} = V(1 + \mu^2) \cos\left(\int_0^t 2\delta dt'\right).$$

Integrating and using the conditions $|a(-\infty)| = 1$, $|b(-\infty)| = 0$, and $|a(t)|^2 + |b(t)|^2 = 1$, we find for the transition probability, at a given impact parameter ρ,

$$T(\rho) = |b(\infty)|^2$$
$$= \left|\sin \int_{-\infty}^{+\infty} dt'' V(t'') \cos\left(\int_0^{t''} (\alpha^2 + 4V^2)^{1/2} dt'\right)\right|^2. \tag{13}$$

We change the variable of integration from time to position x along the rectilinear path of the alkali atom. We write

$$x = vt \text{ and } R^2 = \rho^2 + x^2,$$

where R is the separation of the centers of the al-

kali and halogen atoms, the atoms being closest when $t = 0$. If the transition probability is small, then Eq. (13) can be written

$$T(\rho) = \left| \frac{1}{v} \int_{-\infty}^{+\infty} dx \, V(x) \right.$$

$$\left. \times \cos\left(\frac{1}{v}\int_0^x [\alpha^2(x') + 4V^2(x')]^{1/2} dx'\right) \right|^2,$$

(14)

which is the same as Eq. (3.14) of I. The cross section is found by integrating over impact parameters,

$$\sigma = 2\pi \int_0^\infty \rho T(\rho) \, d\rho.$$

(15)

III. CALCULATION OF CROSS SECTIONS

We use the alkali wave functions from Bates and Damgaard[3] and the halogen negative-ion wave functions from Clementi and McLean[4] and Clementi et al.[5] For V^A we use the attractive Coulomb potential and for V^B the long-range attractive polariza-

tion part of the halogen potential. From Robinson and Geltman[6] we have

$$V^B = -\alpha(1 - e^{-r/r_p})/2(r^2 + r_p^2)^2.$$

Values of α (polarizability) and r_p for chlorine and fluorine negative ions are given in Table I.

The matrix elements $\bar{V}_{ii}$, $\bar{V}_{jj}$, and $\bar{V}_{ij}$ were evaluated with these wave functions and potentials. As in the case of the alkali-metal-oxygen problem of I, $\bar{V}_{jj} \sim 1/R$ at large distances and $\bar{V}_{ii} \ll \omega_{ji}$ everywhere. As in I, $\bar{V}_{ij}$ can be fitted to the functional form $\lambda e^{-\gamma R}$. Values of λ and γ for various pairs of colliding atoms are given in Table II. Plots of $\bar{V}_{ij}$ and $\bar{V}_{kj}$ for the collision of cesium and chlorine are shown in Fig. 1, which is typical of the other pairs of atoms. The matrix elements responsible for charge transfer behave in a way similar to those for alkali-metal-oxygen collisions. Most of the contribution to the transition probability comes from the region where α^2 and $4V^2$ have comparable magnitudes, as can be seen by plotting the integrand in (14) against vt for each ρ (cf. Fig. 7 of I). Applying the method of steepest descent to (14), as in Poluektov et al.,[7] we find

$$T(\rho) = \exp\left(-2^{1/2}\omega/v\right)\{\rho^2 + k_1^2 - k_2^2 + [(\rho^2 + k_1^2 - k_2^2)^2 + 4k_1^2 k_2^2]^{1/2}\}^{1/2}\right) \sin^2\frac{1}{v}\int_{-\infty}^{+\infty} V(x)\,dx,$$ (16)

where $k_1 = \pi/2\gamma$, $k_2 = (1/\gamma)\ln(2\lambda/\Delta\omega)$, and $\Delta\omega = |\omega - 1/R|$ at the value of R for which

$$\alpha^2 = (\omega - 1/R)^2 = 4V^2.$$

The results obtained with (16) are shown in Figs. 2-5.[8] The cross sections for charge transfer from the ground and first-excited ($^2P_{1/2}$) states of the alkali-metal atom are shown by σ_{ij} and σ_{kj}, respectively. In each case the final state is the ground state of halogen negative ion.

IV. ASYMPTOTIC FORMULA

At very low velocities the $\sin^2$ term in (16) oscillates rapidly and can be replaced by its average value $\frac{1}{2}$. Making the transformation

TABLE I. Values of α and r_p for fluorine and chlorine atoms (atomic units).

Ion	α	r_p
Fluorine	4.05	1.5
Chlorine	23.5	2.5

TABLE II. Values of parameters λ and γ for calculating charge-transfer cross sections in alkali-metal-halogen collisions.

System	Transition[a]	λ	γ
Na + F	$i \rightarrow j$	0.0564	0.5980
	$k \rightarrow j$	0.0406	0.4306
Na + Cl	$i \rightarrow j$	0.8168	0.5756
	$k \rightarrow j$	0.2153	0.4515
K + F	$i \rightarrow j$	0.0790	0.5233
	$k \rightarrow j$	0.0304	0.4034
K + Cl	$i \rightarrow j$	0.5431	0.5482
	$k \rightarrow j$	0.1380	0.4112
Rb + F	$i \rightarrow j$	0.0812	0.5174
	$k \rightarrow j$	0.0304	0.3970
Rb + Cl	$i \rightarrow j$	0.4447	0.5293
	$k \rightarrow j$	0.1020	0.3870
Cs + F	$i \rightarrow j$	0.0759	0.5006
	$k \rightarrow j$	0.0276	0.3837
Cs + Cl	$i \rightarrow j$	0.3630	0.5060
	$k \rightarrow j$	0.0981	0.3775

[a]i: alkali ground state; k: alkali first-excited state; j: halogen negative-ion ground state.
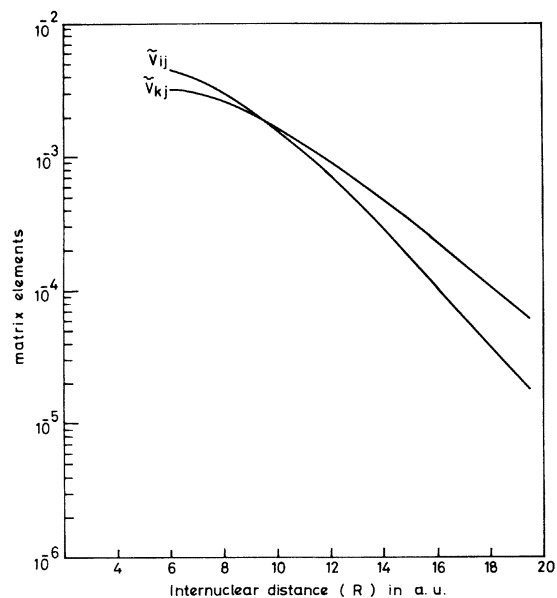
FIG. 1. Magnitudes of matrix elements $\tilde{V}_{ij}$ and $\tilde{V}_{kj}$ for cesium-chlorine collisions. Atomic units are used.
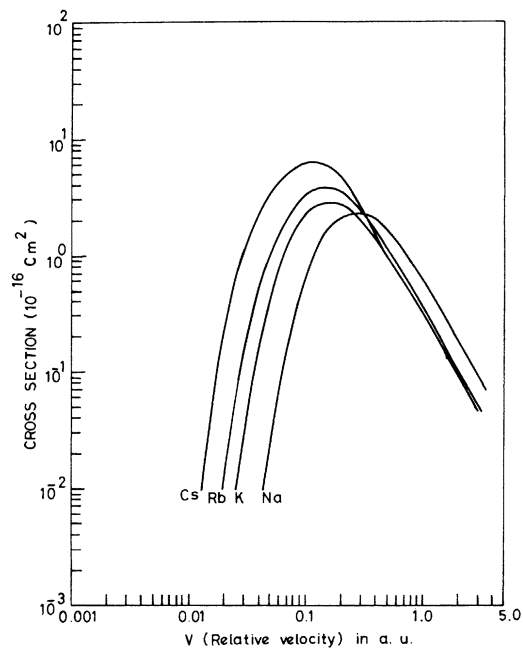

FIG. 3. Charge-transfer cross sections (σ_{ij}) for Na-F, K-F, Rb-F, and Cs-F collisions as functions of the relative velocity v in atomic units.
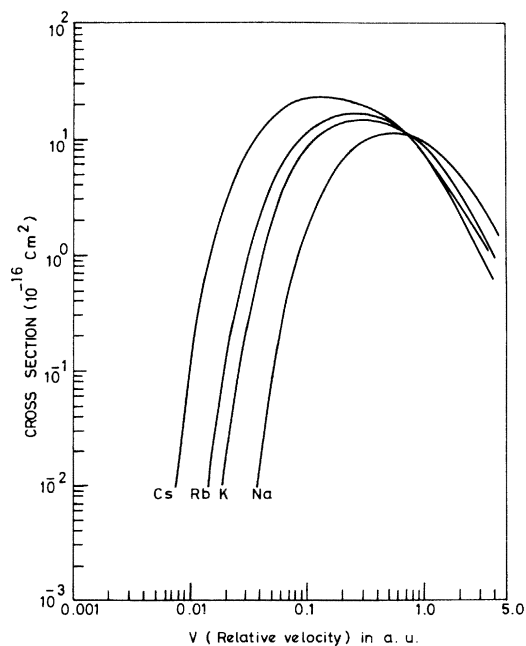

FIG. 2. Charge-transfer cross sections (σ_{ij}) for Na-Cl, K-Cl, Rb-Cl, and Cs-Cl collisions as functions of the relative velocity v in atomic units.
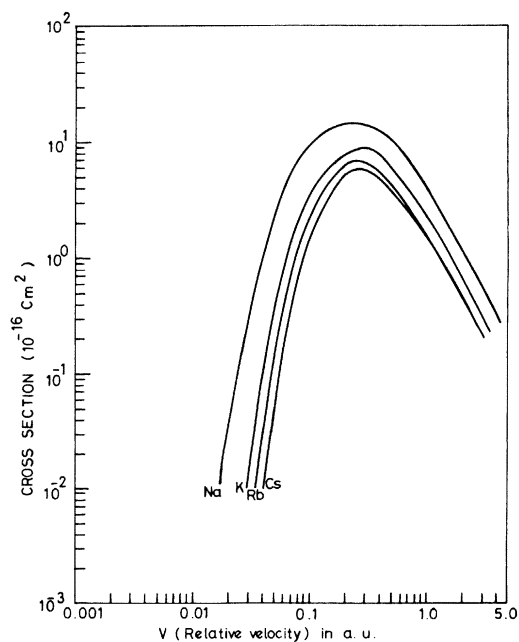

FIG. 4. Charge-transfer cross sections (σ_{kj}) for Na-Cl, K-Cl, Rb-Cl, and Cs-Cl collisions as functions of the relative velocity v in atomic units.

$$\rho^2 + k_1^2 - k_2^2 = K^{1/2} \tan\theta,$$

where $K = 4k_1^2 k_2^2$, we obtain from Eq. (15)

$$\sigma(v) = \frac{\pi K^{1/2}}{2} \int_{\tan^{-1}\varphi}^{\pi/2} \exp[-J(\tan\theta + \sec\theta)^{1/2}] \sec^2\theta \, d\theta,$$

where

$$J = MK^{1/4}, \quad M = 2^{1/2}\omega/v, \quad \varphi = (k_1^2 - k_2^2)/K^{1/2}.$$

Letting $\tan\theta + \sec\theta = U^2$, we have

$$\sigma(v) = \frac{\pi K^{1/2}}{2} \left(\frac{e^{-JX}}{J^2}(JX + 1) + \frac{1}{X^2} E_3(JX) \right),$$

where $X = [\varphi + (1 + \varphi^2)^{1/2}]^{1/2}$ and E_3 is the exponential integral. At large values of the argument JX (i.e., when $v \to 0$), $E_3 \sim e^{-JX}/JX$. Thus $\sigma(v)$ can be written

$$\sigma(v) = \frac{\pi v^2}{4\omega^2} \exp(-\omega X K^{1/4} v) \left(1 + \frac{2^{1/2}\omega K^{1/4}}{X^3} \frac{1}{v}\right),$$

which has the same functional dependence on v and ω as found by Bates.[2]

V. RESULTS AND DISCUSSION

The salient features of the charge-exchange cross sections for alkali-metal–halogen collisions in the two-state approximation are very similar to those for the alkali-metal–oxygen collisions of I. The matrix elements responsible for charge exchange have the same functional form. At low velocities, the cross sections increase with v to a maximum and thereafter decrease as $1/v^2$, as expected from the Born approximation.[8] The asymptotic formula obtained here confirms this functional behavior at low velocities. The cross sections σ_{ij} in both the alkali-metal–halogen and alkali-metal–oxygen cases have the same order of magnitude. However, the maxima in the cross sections occur at higher velocities in the case of alkali-metal–halogen collisions. The σ_{kj} for alkali-metal–halogen collisions are markedly smaller than for alkali-metal–oxygen collisions. A dis-
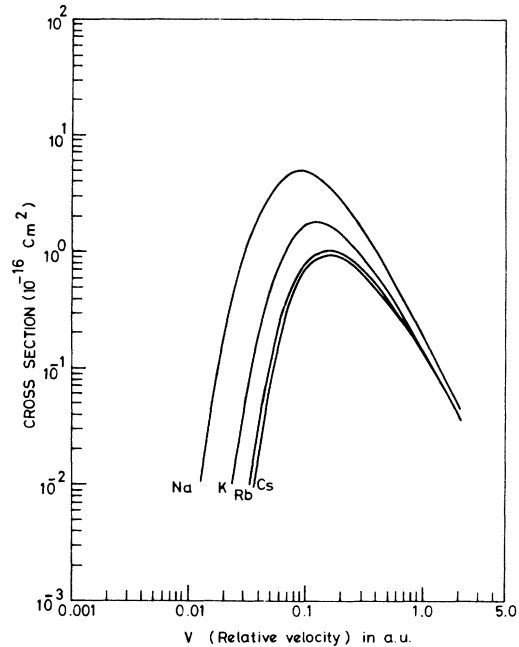
FIG. 5. Charge-transfer cross sections (σ_{kj}) for Na-F, K-F, Rb-F, and Cs-F collisions as functions of the relative velocity v in atomic units.

tinctly different feature in the present studies, as seen from Figs. 4 and 5, is the decrease in σ_{kj} in going from Na to Cs, the reverse of the trend for alkali-metal–oxygen collisions. This behavior is due to the fact that electron affinities of the halogen atoms (Cl$^-$ = 3.61 eV, F$^-$ = 3.45 eV) are much higher than that of oxygen (O$^-$ = 1.46 eV). Hence the energy difference $|\omega_{kj}|$ increases for alkali-metal–halogen collisions as one goes from Na to Cs, while it decreases for alkali-metal–oxygen collisions. This trend is reflected in the cross sections obtained in the present work.

ACKNOWLEDGMENTS

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