Resonant charge transfer in collisions between positive ions

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(Received 21 January 1994)

We present a numerical evaluation of the resonant charge-transfer cross sections for ions of various positive charges. In the calculations we introduce trajectory parameters through the expression for the instantaneous velocity of the projectile. Subsequent analysis reveals the existence of a natural scaling law by which cross sections of ion-ion collisions can be generated from the isoelectronic ion-atom charge-exchange cross section. We obtain a set of simple formulas useful for a semiquantitative description of the features of such cross section curves and we discuss the oscillatory structure of the cross sections.

PACS number(s): 34.70.+e

INTRODUCTION

The resonant charge-transfer process

$$X^+ + X \Rightarrow X + X^+ \tag{1}$$

in the collision of an ion X^+ with its parent atom has received considerable attention and the magnitude and variation of the cross section with collision energy have been calculated for many ion-atom pairs [1–7]. The cross sections oscillate about a mean which decreases monotonically with increasing energy.

The ion and the atom may approach along either of the two potential energy curves, one, $\varepsilon_g(R)$, corresponding to the gerade state of the molecular ion $X_2{}^+$ and the other, $\varepsilon_u(R)$, corresponding to the ungerade state, where R is the internuclear distance. Except at very low energies the nuclear trajectories may be taken to be linear and the cross section is determined by the difference potential $\Delta\varepsilon(R) = \varepsilon_u(R) - \varepsilon_g(R)$. In resonant charge-transfer collisions of positive ions with positive ions

$$X^{Z+} + X^{(Z-1)+} \Rightarrow X^{(Z-1)+} + X^{Z+}, \tag{2}$$

the nuclear motion takes place in the Coulomb field $Z(Z-1)/R$ of the interacting ions and the assumption of linear trajectories must be discarded. As shown by the calculations of Bardsley *et al.* [8] the Coulomb repulsion introduces an effective energy threshold below which the charge-transfer process is ineffective. The approximations made by Bardsley *et al.* suppress any oscillatory structures that might be present in the cross sections.

We extend the study of the resonant charge transfer in positive ion-ion collisions by carrying out more accurate calculations and we find that the oscillatory structures persist although they are less pronounced than in the ion-atom cases. We also seek a scaling procedure for the collision energy and the cross sections in an attempt to construct a universal curve from which useful estimates can be made of the resonant charge transfer involving any positive ion. We find that by multiplying each ion-atom cross section by appropriate "trajectory factors" the cross sections of a series of ion-ion systems may be generated.

THEORY AND CALCULATIONS

The charge-exchange cross section can be written in the form [1,2]

$$\sigma(E) = 2\pi \int_0^\infty \rho d\rho \sin^2\{\zeta(\rho)\}, \tag{3}$$

where $\zeta(\rho)$ is the difference in phase arising in the elastic scattering by the potentials $\varepsilon_g(R)$ and $\varepsilon_u(R)$ evaluated at the impact parameter ρ. If in evaluating the nuclear trajectories we adopt a common potential $\varepsilon(R) = \frac{1}{2}\{\varepsilon_u(R) + \varepsilon_g(R)\}$, the semiclassical formula for the phase difference is

$$\zeta(\rho) = \int_{R_t}^\infty \frac{\Delta\varepsilon(R)}{v_R} dR, \tag{4}$$

where R_t is the classical distance of closest approach for the nuclei in the potential $\varepsilon(R)$, v_R is the radial velocity at R, given by

$$v_R = \left\{ \frac{2}{m}\left[E - \frac{\rho^2}{R^2}E - \varepsilon(R)\right] \right\}^{1/2}, \tag{5}$$

m is the ion mass, and E is the initial energy of the projectile. For the positive ion-ion collisions the potential $\varepsilon(R)$ is dominated by the Coulomb repulsion term $Z(Z-1)/R$ and the use of a common potential is valid down to low velocities.

For the evaluation of the radial velocity of hydrogenlike ions $\varepsilon_g(R)$ and $\varepsilon_u(R)$ can be obtained directly from the calculations for $H_2{}^+$ by scaling the energy in units of Z^2 and length in units of Z^{-1} and adding the Coulomb repulsion. For lithium ion-atom collisions we used the

TABLE I. Model potential parameters for lithiumlike ions.

Ion	a_1	a_2	a_3	a_4	a_5	α_c
Be^{2+}	3.7085113	1.6302359	1.8415093	0.0216971	-0.1198800	0.1932634
B^{3+}	4.7625048	1.7050000	3.9110000	0.1949878	-1.0000080	0.1932634
C^{4+}	4.7625048	1.7050000	3.9110000	0.5350000	-0.9899999	0.1932634
N^{5+}	2.5061870	1.6802350	1.8415090	0.9750000	-0.1150000	0.1919999
O^{6+}	3.7625045	1.7050000	3.9110000	1.2557319	-1.0000000	0.1923000

actual electronic energy $\varepsilon(R) = \frac{1}{2}\{\varepsilon_u(R) + \varepsilon_g(R)\}$, and for the lithiumlike ions, we assumed that in the determination of v_R from Eq. (5) the potential $\varepsilon(R)$ could be taken equal to the Coulomb repulsion.

The electron-electron interaction within the lithiumlike ions prevents a simple scaling of the energy $\varepsilon_{u,g}(R)$ analogous to the hydrogenlike series. We calculated $\Delta\varepsilon(R)$ numerically using the Holstein-Herring formula [10–13], coupled to a model potential description of the motion of the valence electron [14,15]. The model potential for $X^{(Z-1)+}$ has the form

$$V(r) = -\frac{1}{r}[N - 2 + 2e^{-a_1 r} - (a_4 + a_5 r)e^{-a_3 r}] - \frac{\alpha_c}{2r^4}[1 - e^{-a_2 r}], \quad (6)$$

where N is the charge of the nucleus, α_c is the core polarizability and a_1, a_2, a_3, a_4, and a_5 are parameters chosen so that the eigenvalues corresponding to $V(r)$ match the energy levels of $X^{(Z-1)+}$. The values of these parameters for Be^+, B^{2+}, C^{3+}, N^{4+}, and O^{5+} are listed in Table I.

The Holstein-Herring formula for the difference potential $\Delta E(R)$ is

$$\Delta\varepsilon(R) = -2\int_\Omega \chi_p \nabla\chi_p \cdot d\Omega, \quad (7)$$

where χ_p is a localized wave function and the integral is evaluated over the midplane Ω between the two nuclei. It is asymptotically exact. We adopted for χ_p the first-order polarized wave function corresponding to the perturbation of $X^{(Z-1)+}$ by the electric field generated by the presence of a charge Z [12]. The resulting values of $\Delta\varepsilon(R)$ as shown in Fig. 1 are exponentially decreasing functions of R.

The calculated cross sections for incident hydrogenlike and lithiumlike ions are presented in Figs. 2 and 3. Because of our more detailed calculations of the exchange interactions and a more complete treatment of the trajectories, our cross sections differ from those of Bardsley *et al.* [8] and in no case by more than a factor of 2. They differ also in containing oscillatory structures though the oscillations are less pronounced than for the ion-atom cases.

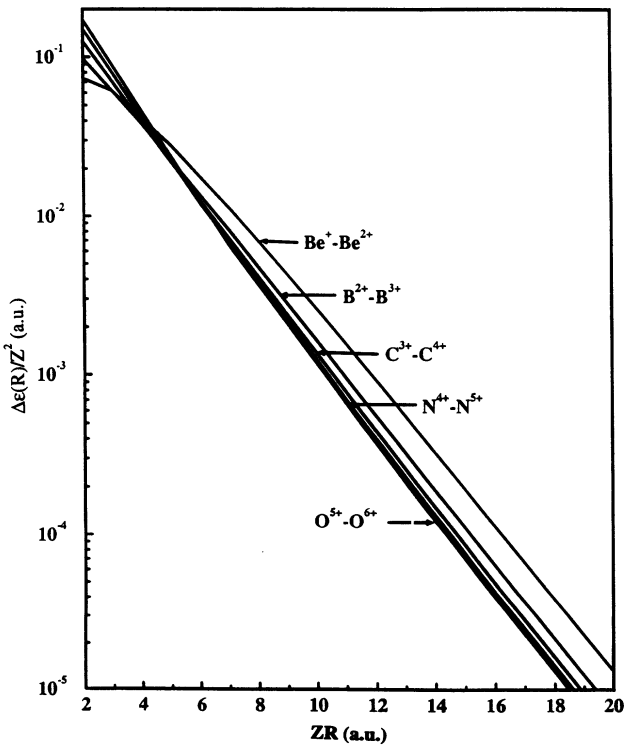

FIG. 1. The exchange energy $\Delta\varepsilon(R)/Z^2$ of the lithiumlike ions evaluated using Eq. (7) plotted as functions of ZR.

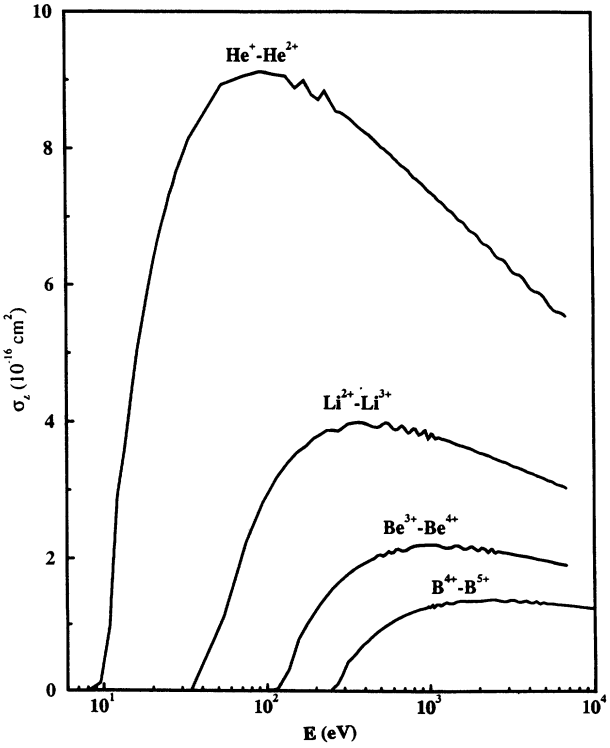

FIG. 2. The symmetric charge-transfer cross sections $\sigma_x(E)$ for the ions belonging to the hydrogenlike series.

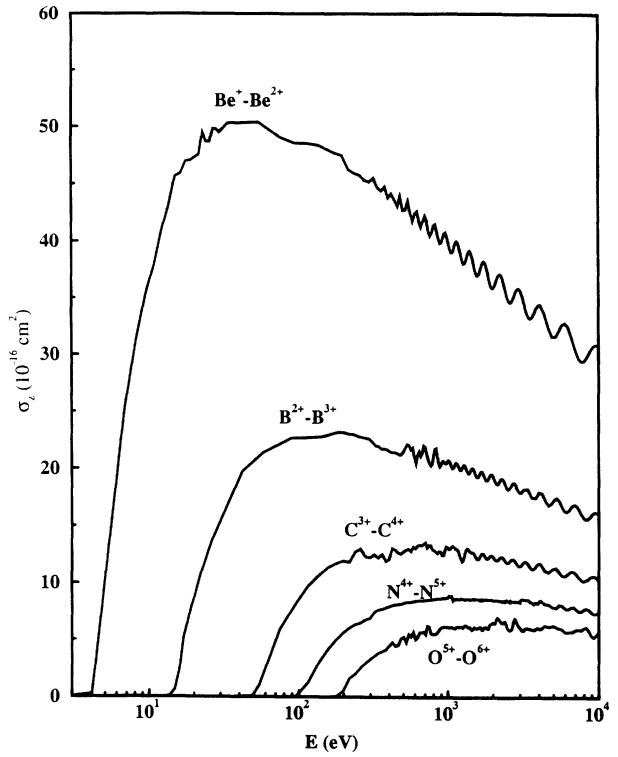

FIG. 3. The symmetric charge-transfer cross sections $\sigma_z(E)$ for the ions belonging to the lithiumlike series.

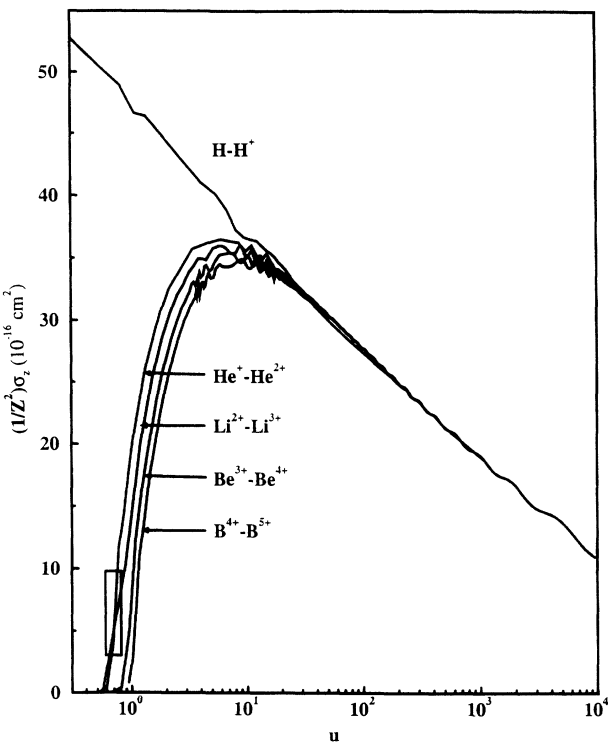

FIG. 4. The scaled symmetric charge-transfer cross sections for hydrogenlike ions. The rectangular box highlights the crossing of the He^+-He^{2+} and Li^{2+}-Li^{3+} cross section curves. All cross sections coalesce into a single curve at high energies.

UNIVERSAL CURVE

If it were not for the influence of the Coulomb repulsion, the cross sections for the hydrogenlike ions would scale exactly to yield

$$\sigma_z(E) = \frac{1}{Z^2}\sigma_h\left(\frac{m_h}{m_z}\frac{E}{Z^2}\right), \tag{8}$$

where σ_h is the cross section for H^+-H collision. For the lithiumlike sequence, Eq. (8) may be replaced by

$$\sigma_z(E) = \frac{I_l}{I_z}\sigma_l\left(\frac{m_l}{m_z}\frac{E}{I_z}\right), \tag{9}$$

where I_l is the ionization potential of lithium, I_z is the ionization potential of the lithiumlike ion with charge Z-1, and σ_l is the cross section of the Li-Li^+ collision.

The cross sections evaluated numerically and scaled according to Eqs. (8) and (9) are shown in Figs. 4 and 5 as functions of the dimensionless energy $u = \frac{m_{h,l}}{m_z}\frac{E}{I_z}$. At high energies where the Coulomb repulsion is relatively less important, the scaled cross sections for each sequence tend to the corresponding limiting curve. At small energies the curves are distinct and the scaling fails.

To interpret the behavior of the cross sections, we rewrite Eqs. (3) and (4) using the radial coordinate R_t for the turning point as the independent variable instead of the impact parameter. Thus with $\rho^2 = R_t^2\left\{1-\frac{\epsilon(R_t)}{E}\right\}$, $\sigma(E)$ may be written

$$\sigma(E) = 2\pi\int_{R_h}^{\infty}\sin^2\zeta(R_t)\,T(E)\,R_t dR_t, \tag{10}$$

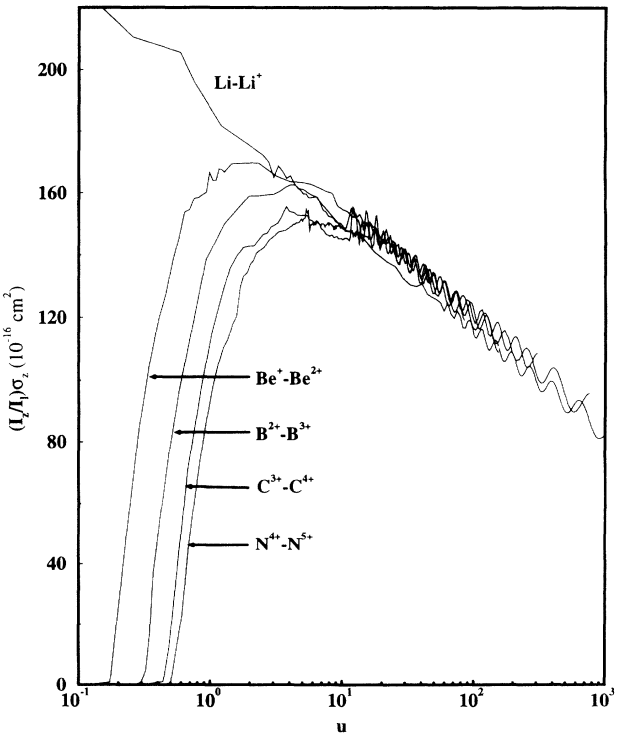

FIG. 5. The scaled symmetric charge-transfer cross sections for lithiumlike ions. The cross sections coalesce at high energies, though not as completely as in the hydrogenlike series.

where R_h is the turning point for a head-on collision with $\rho = 0$ and $T(E)$ is a trajectory factor,

$$T(E) = 1 - \frac{\varepsilon(R_t)}{E} - \frac{\varepsilon'(R_t)R_t}{2E}. \tag{11}$$

The phase difference $\zeta(R_t)$ is given by

$$\zeta(R_t) = \tfrac{1}{v}\int_{R_t}^{\infty} \frac{\Delta\varepsilon(R)RdR}{\left[R^2\left(1-\frac{\varepsilon(R)}{E}\right) - R_t^2\left(1-\frac{\varepsilon(R_t)}{E}\right)\right]^{\frac{1}{2}}}, \tag{12}$$

where v is the relative velocity. If we consider the pure Coulombic case, $\varepsilon(R) = \frac{Z(Z-1)}{R}$, $R_h = 2\tilde{r} = \frac{Z(Z-1)}{E}$, and we obtain

$$T(E) = 1 - \tilde{r}/R_t \tag{13}$$

and

$$\zeta(R_t) = \frac{1}{v}\int_{R_t}^{\infty} \frac{\Delta\varepsilon(R)RdR}{[(R-\tilde{r})^2 - (R_t-\tilde{r})^2]^{\frac{1}{2}}}. \tag{14}$$

For head-on collision R_t in Eq. (14) is identical to $R_h = \frac{Z(Z-1)}{E}$.

The "asymptotic theory" can be used for further simplification of the above equations. Because the exchange interaction decreases exponentially with distance the pre-exponential factor in the phase integral (12) can be written as a Taylor series expansion about the turning point. By rewriting $R = R_t + y$ Eq. (14) reduces in the asymptotic region to

$$\begin{aligned}\zeta(R_t) &= \frac{1}{v}\int_0^{\infty} \frac{\Delta\varepsilon(R_t+y)(R_t+y)dy}{\left[(R_t+y)^2\left(1-\frac{\varepsilon(R_t+y)}{E}\right) - R_t^2\left(1-\frac{\varepsilon(R_t)}{E}\right)\right]^{\frac{1}{2}}} \\ &\cong \frac{\Delta\varepsilon(R_t)\sqrt{R_t}}{\sqrt{2}v\left(1-\frac{\varepsilon(R_t)}{E}-\frac{\varepsilon'(R_t)R_t}{2E}\right)^{\frac{1}{2}}}\int_0^{\infty}\frac{e^{-y/r_b}dy}{\sqrt{y}} \\ &= \sqrt{\frac{\pi}{2}}\frac{\Delta\varepsilon(R_t)\sqrt{R_t r_b}}{v}T^{-\frac{1}{2}}(E),\end{aligned} \tag{15}$$

where $r_b = 1/\sqrt{2I_z}$ is the effective Bohr radius. It is the presence of the trajectory factor that precludes the invariance of the phase shift which is a required condition for the success of the scaling procedure. The scaling procedure fails because the trajectory factor is a function of energy. In the high-energy limit, $T(E)$ tends to unity and the scaling is exact.

To evaluate (10) we make use of the Firsov approximation [16] in which $\sin^2\zeta(R_t)$ is taken to be equal to 0.5 for all the trajectories for which $\zeta(R_t)$ is less than a small number, often taken to be 0.28 [8,16], and zero otherwise. If R_f is the corresponding value of R_t at which $\zeta(R_t = R_f) = 0.28$, we may write for the ion with charge Z

$$\begin{aligned}\sigma_z(E) &= \frac{\pi}{2}R_f^2(Z)\left[1 - \frac{2\tilde{r}}{R_f(Z)}\right] \\ &= \left(\frac{I_0}{I_z}\right)\frac{\pi}{2}R_{f0}^2\left[1 - \left(\frac{I_z}{I_0}\right)^{1/2}\frac{Z(Z-1)}{ER_{f0}}\right].\end{aligned} \tag{16}$$

In the second line of the above equation we use the scaling law for the length to write the "Firsov radius" $R_f(Z)$ of the ion in terms of the corresponding value of the hydrogen or lithium atom-ion system. The values corresponding to the atom-ion systems are denoted by a subscript 0. The resulting equation shows how the cross section for any ion system of a series can be derived from the "Firsov cross section" of the first member of the family. The accuracy of such predictions clearly improves with the accuracy of the Firsov cross section. At this point we replace this approximate value by the best available ion-atom charge-exchange cross section. This could be the result of an experiment or of a better *ab initio* calculation as in the present case. Expressing the energy in the dimensionless units of u, Eq. (16) is rewritten as

$$\left(\frac{I_z}{I_0}\right)\sigma_z(u) = \sigma_0\left[1 - \sqrt{\frac{\pi}{2\sigma_0}}\frac{Z(Z-1)}{u}\left(\frac{m_0}{m_z}\right)\left(\frac{I_0}{I_z}\right)^{1/2}\right]. \tag{17}$$

This procedure produces a generalized "Firsov formula." As the cross section curves of the ion-atom collision in general possess an oscillatory structure the cross sections for any other member generated from them by a multiplication of the appropriate trajectory factor within the square brackets of Eq. (17) exhibit similar structures. The equations are valid for any series and can be used as long as the cross section for the first member is known.

The Z dependence of the threshold of the unscaled cross section can be obtained approximately by equating the terms within the square brackets of Eq. (16) to zero. To a first approximation the threshold energy is given by

$$E \propto Z(Z-1)\left(\frac{m_z}{m_0}\right)\left(\frac{I_z}{I_0}\right)^{1/2}.$$

The position of the threshold depends on the charge and the mass of the ion. A clear manifestation of mass dependence is evident in Fig. 4. There the mass effect causes the crossing of the Li^{2+}-Li^{3+} and the He^{+}-He^{2+} curves.

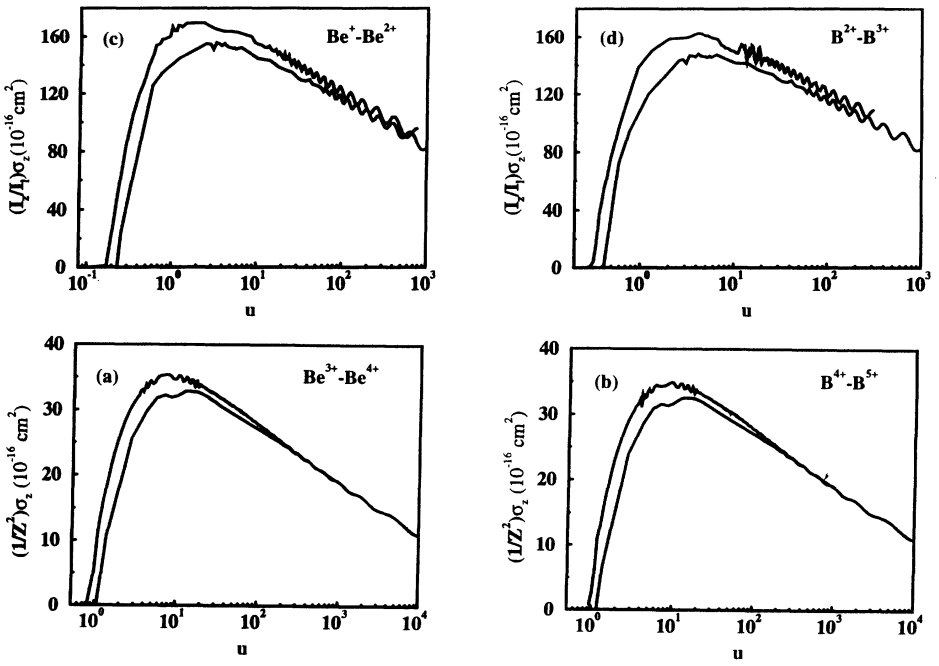

FIG. 6. Comparison of the analytical calculation of the scaled cross sections from Eq. (17) with numerical evaluation (a) Be^{3+}-Be^{4+}, (b) B^{4+}-B^{5+}, (c) Be^{+}-Be^{2+}, and (d) B^{2+}-B^{3+}. In each case the upper curve is the numerically evaluated cross section and the lower curve is the analytical result.

The masses of the ions with large Z are proportional to Z, $m_z \sim \beta m_0 Z$, where β is a constant. Then Eq. (17) shows that for ions with large Z the dimensionless threshold energy is independent of the charge Z. Thus there is a theoretical upper limit $u_{\rm th}$ for the scaled cross section threshold; $u_{\rm th} \simeq \frac{1}{\beta}\sqrt{\frac{\pi}{2\sigma_{0\rm th}}}$. The positions of the maxima of the scaled curves can be estimated using the equation

$$\frac{d\sigma(u)}{du} = 0 \Rightarrow u^2\sigma_0'(u)\sigma_0^{1/2} - \frac{Z(Z-1)}{2}\left(\frac{I_0}{I_z}\right)^{1/2}\frac{m_0}{m_z}$$

$$\times\left[\frac{u}{2}\sigma_0' - \sigma_0\right] = 0. \qquad (18)$$

In order to assess the accuracy of the analytic expressions we compare their predictions with our numerical calculations as shown in Fig. 6. The agreement is excellent, although the assumption that all the exchange processes are limited to a critical sphere systematically leads to an underestimate of the cross sections and causes a slight discrepancy with the numerical results. The cross sections exhibit distinct oscillatory patterns at large values of the ion energies. The oscillations are periodic functions of inverse velocity with period proportional to $1/Z$ and amplitude proportional to $1/Z^2$.

For the hydrogenlike ion group the oscillations are rather smooth. The oscillations scale exactly and the results for all the ions coincide at high energies. The oscillations of the Li-Li^+ cross section are far stronger than in the H-H^+ cross section. The same trend is apparent in the cross sections of the ions of the corresponding series. Because of the trajectory effect in the cross section calculation the amplitude of the oscillations is reduced at high energies of collision and for small energies the oscillations disappear, but the inclusion of the trajectory factor does not remove the oscillatory structure of the ion-ion cross sections completely. The phase difference $\zeta(\rho)$ remains almost invariant at sufficiently high scaled energies so that the oscillations of the various curves almost coincide. For the scaled curves of the calculated cross sections the maxima occur at about ten times the threshold energy as suggested by Eq. (18).

Our formulas may be useful in the planning of experimental studies of ion-ion charge-exchange cross sections. For example, oscillations of the charge-transfer cross sections have been measured [17] for the atom-ion Mg-Mg^+, Be-Be^+, Ca-Ca^+, and Sr-Sr^+ collisions and may be expected for the respective isoelectronic ion series. The universal curve that we obtained should be useful in interpreting experimental results for various ion pairs.

ACKNOWLEDGMENT

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy.

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