Symmetric resonant charge transfer in $H^+ + H$ and $He^{2+} + He$ collisions at extremely low energies

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Symmetric resonant charge transfer (RCT) in $H^+ + H$ and $He^{2+} + He$ collisions has been investigated in the ultralow-collision-energy range 10^{-3}–10^{-7} eV. The RCT cross section has been computed by partial-wave expansion in the molecular-orbital expansion method within the fully quantum-mechanical formalism. The calculated RCT cross sections become constant below $E \simeq 10^{-6}$ eV, corresponding to a scattering length of $\sim 6a_0$ and $\sim 2a_0$ for H_2^+ and He_2^{2+}, respectively.

Resonant charge transfer (RCT) for one-electron transfer in symmetric $H^+ + H$ collisions, and two-electron transfer in symmetric $He^{2+} + He$ collisions, has been a popular subject of theoretical[1–13] as well as experimental[14–18] investigations since the early 1920s, when quantum mechanics was being developed. With regard to the theoretical investigation of RCT collisions, almost all the available theoretical approaches ranging from perturbation[1,2,4,5] to close-coupling[3,4,6–13] methods, and based on either a semiclassical or fully quantum-mechanical formalism, have been applied to these processes as stringent and convenient tests of the theory over quite a wide energy range, from a few meV to a few MeV. Owing to these efforts, the fundamental collision dynamics for the RCT process is now well known, and qualitative as well as quantitative agreement of calculated RCT cross sections with measurements is generally very good. For low-energy collisions, the molecular-orbital (MO) expansion method [or the perturbed-stationary-state (PSS) method] is considered to be appropriate for the study of elastic and inelastic phenomena in ion-atom collisions. Below 100 eV, the RCT process is the dominant state-changing event in symmetric ion-atom collisions (more than 5 orders of magnitude larger in terms of cross section than any other inelastic state-changing process). In the MO (PSS) picture, the RCT process is determined by two electronic states which are of different symmetries (one gerade $1\Sigma_g$ and the other ungerade $1\Sigma_u$) but both of which correlate to the asymptotic ground state of the system. Although these two states do not couple through the usual dynamical process, the corresponding internuclear potentials induce the charge transfer due to the fact that the quantum-mechanical phase factors for each trajectory evolve differently as functions of the time.

Several attempts to investigate the RCT in $H^+ + H$ and $He^{2+} + He$ collisions using the MO expansion method have been reported at energies down to the range of 10^{-3}–10^{-2} eV. For both systems, the shape of the calculated RCT cross section shows an increasing trend, with decreasing energy, at the lowest energy studied so far. This trend is partly interpreted by the semiempirical formula[10] $\sigma \sim (B - \ln v)^2$, which qualitatively describes the behavior of RCT cross sections at low-to-intermediate collision velocities v. To the best of our knowledge, no experimental or theoretical investigations have been reported for collision energies below $\sim 10^{-3}$ eV. Our main aim in this paper is to report the results of applying the standard MO approach to symmetric RCT cross sections in the ultralow energy range, extending down $\sim 10^{-7}$ eV.

In a sense there is nothing fundamentally new in this paper. It is well known from quantum-mechanical considerations that the RCT cross section will turn over at low energies and remain finite as $E \to 0$, and only a single partial wave ($l=0$) continues to contribute. However, the precise shape of the cross section in the ultralow energy regime has, to the best of our knowledge, not been previously reported. We find it to be of interest.

The theoretical method used in the adiabatic MO (PSS) approach familiar in ion-atom collision theory,[3,13] is here applied in a fully quantum-mechanical treatment. The gerade and ungerade phase shifts are obtained by solving the uncoupled radial Schrödinger equations

$$\frac{d^2X_i(R)}{dR^2} + \left[2\mu E - \frac{l(l+1)}{R^2} - 2\mu W_i(R)\right] X_i(R) = 0 \ , \tag{1}$$

for the asymptotic form of the radial functions $X_i(R)$, where μ is the reduced mass of heavy particles and the $W_i(R)$ represents the adiabatic potentials for the gerade ($i=g$) and ungerade ($i=u$) states. Then, the RCT cross section can be calculated from the corresponding phase shifts, η_l^i, from the equation (see, for example, Ref. 13),

$$\sigma^{\mathrm{RCT}} = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2(\eta_l^g - \eta_l^u) \ , \tag{2}$$

where k describes the wave number with $k = \{2\mu[E - E(\infty)]\}^{1/2}$. The radial Schrödinger equations (1) have been solved numerically to obtain phase shifts by the log-derivative method.[19] Adiabatic potential curves for the $1\Sigma_g$ and $1\Sigma_u$ states of the H_2^+ system have been calculated "exactly" by the method of Bates *et al.*[20] including the diagonal matrix elements of the energy operator of the nucleus[21] and those of the He_2^{2+} system have been obtained by the full configuration interaction

method with the Slater-type-orbital bases.[22]

Figure 1 illustrates the potential-energy differences, $\Delta E(R)=E(1\Sigma_u)-E(1\Sigma_g)$, for both the H_2^+ and He_2^{2+} systems as functions of internuclear distance R. For the H_2^+ system the $1\,^2\Sigma_g$ and $1\,^2\Sigma_u$ states correlate with He^+ $(1s)$ at -2.0 a.u. and $He^+(n=2)$ at -0.5 a.u., respectively, in the united atom limit $R\rightarrow 0$, although these states are asymptotically degenerate, representing an $H^+ + H(1s)$ state. No curve crossings occur for the $1\,^2\Sigma_g$ and $1\,^2\Sigma_u$ energy curves at any internuclear separation. Hence, the energy difference between the $1\,^2\Sigma_u$ and $1\,^2\Sigma_g$ states decreases exponentially as R increases. The situation is more complex for the He_2^{2+} system. The $(1s\sigma_g 2p\sigma_u)\,^1\Sigma_u^+$ state correlates with $Be^{2+}(1s2p\,^1P)$ at $R=0$ and $He^{2+} + He(1s^2)$ at $R=\infty$, and no avoided crossing for this state exists at any R value. The $(2p\sigma_u^2)\,^1\Sigma_g^+$ state exhibits a narrow avoided crossing with the $(1s\sigma_g 2s\sigma_g)\,^1\Sigma_g^+$ state at $R\sim 1.35$ a.u., with an energy gap between the two of 0.085 a.u. This and subsequent avoided crossings with the $(2p\sigma_u^2)\,^1\Sigma_g^+$ state are now well known to be diabatic and to play an important role in interpreting the collision dynamics for the charge transfer in $He^+ + He$ as well as $He^{2+} + He$ collisions at the intermediate energy (see Lichten[8]). However, at a sufficiently low energy, such as that of the present work, the avoided crossing with the $(2p\sigma_u^2)\,^1\Sigma_g$ state is adiabatic, resulting in a correlation of the $Be^+(1s2s)$ state at $R=0$ with the $He^{2+} + He(1s^2)$ state at $R=\infty$.

Due to this sharp avoided crossing explained above, the energy difference ΔE between the Σ_g and Σ_u states that describe the collision shows a prominent maximum around $R\sim 1.35$ a.u., and decreases at smaller and larger values of R. However, since the energy of the $Be^+(1s2s)$ state is lower than that of the $Be^+(1s2p)$ state, the energy difference passes through zero at small R before increasing again to 0.19 a.u. at $R=0$. The energy difference for the He_2^{2+} system falls off much faster with respect to R than that of the H_2^+ system. Since the energy range of present interest lies below 10^{-4} eV, the distance of closest approach of the colliding partners is relatively larger than $\sim 5a_0$. Therefore, in the present study, the regions of R where $\Delta E\simeq 0$ and $\Delta E\cong$ max play no role in the RCT collision dynamics.

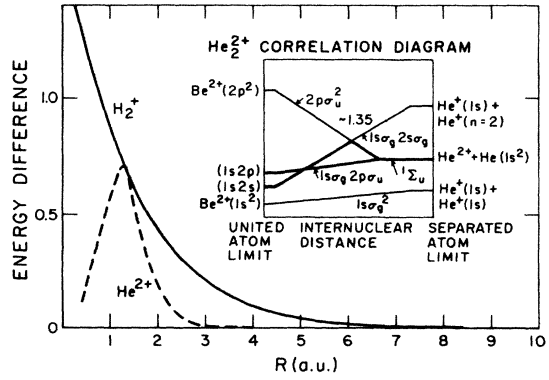

FIG. 1. Energy difference between gerade and ungerade states. A schematic correlation diagram for the He_2^{2+} is also shown. States used in the calculation are indicated in bold lines.

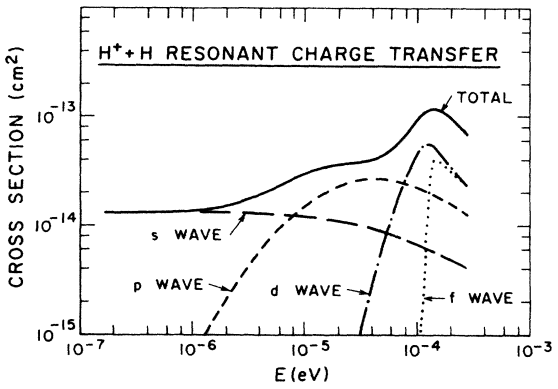

FIG. 2. $H^+ + H$ resonant charge-transfer cross sections vs collision energy. Contribution for each partial wave is shown.

Figures 2 and 3 depict the symmetric RCT cross section for the H_2^+ and He_2^{2+} systems, respectively, at collision energies from 10^{-7} to 10^{-3} eV. Individual partial-wave contributions to the RCT cross section are also included. For the H_2^+ system, the cross section exhibits a maximum ($\sim 1.2\times 10^{-13}$ cm^2) around $E\sim 2\times 10^{-4}$ eV and then decreases, with some structure, in the 10^{-4}–10^{-5} eV region, until it reaches a constant value ($\sim 1.3\times 10^{-14}$ cm^2) below $E\sim 10^{-6}$ eV. Below 10^{-6} eV, the cross section becomes a constant, consisting solely of an s wave ($l=0$) contribution. The gerade and ungerade s-wave phase shifts η_l^g and η_l^u (radians) have been computed to be 1.494, 2.487×10^{-4}, and 0.873, 2.523×10^{-5} for $l=0$ and 1, respectively, at $E=2.7\times 10^{-9}$ eV. These are of sufficient convergence in partial waves. The structure observed in the RCT cross section around $E=4\times 10^{-5}$ eV is due to a growing p wave ($l=1$) contribution and the sharp rise near $E=8\times 10^{-5}$ eV results from the d wave ($l=2$) contribution. Our calculated results at $E\gtrsim 10^{-4}$ eV are in good agreement (within 10%) with the fully quantum-mechanical calculation of Hunter and Kuriyan.[13]

Next, we consider the He_2^{2+} cross sections, which are given in Fig. 3. The overall energy dependence of the

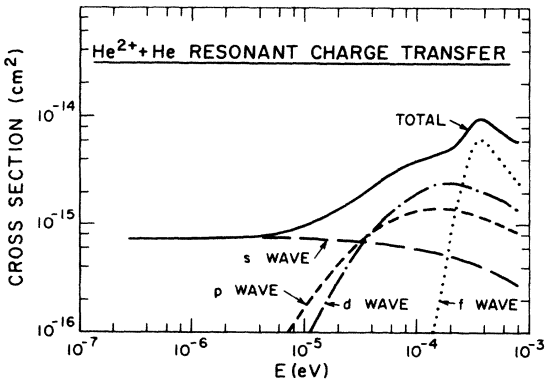

FIG. 3. $He^{2+} + He$ resonant charge-transfer cross sections vs collision energy. Contribution for each partial wave is shown.

RCT cross section for the He_2^{2+} system is quite similar to that of the H_2^+ system. However, the RCT cross sections for the two systems differ in detail. For example, the magnitude of the cross section is an order of magnitude smaller for the He_2^{2+} system, attaining a maximum value of $\sim 1\times 10^{-14}$ cm^2 at $E\sim 3.5\times 10^{-4}$ eV. This difference relates most directly to the fact that the energy difference $\Delta E(R)$ for the He_2^{2+} system is much smaller at the distances ($R \gtrsim 3a_0$) relevant at these collision energies as compared to that of the H_2^+ system. In other words, a difference in polarization may play a role for smaller cross sections for He_2^{2+} relative to H_2^+. Because of these, the phase difference between the gerade and ungerade phase shifts would not be developed enough. In addition, the structure observed in the cross section is not so marked in this case. This is because the p- and d-wave contributions are relatively similar in the magnitude of their energy dependence. At the maximum of the cross section, the f wave seems to be a dominant source in the He_2^{2+} system, whereas it is the d wave in the H_2^+ system. The gerade and ungerade phase shifts η_l^g and η_l^u (radians) have been obtained by ensuring sufficient convergence with 3.669, 1.459×10^{-3}, and 2.760, 5.463×10^{-4} for $l=0$ and 1, respectively, at 2.8×10^{-8} eV.

This obviously indicates that only the s wave contributes to the RCT cross section at large impact parameters below 10^{-6} eV. Although no other theoretical or experimental data are available in the energy range matched with the present result, extrapolation of our result calculated at highest energy toward higher energies seems to be about a factor of 2 larger than that of Ferguson *et al.*'s[4] lowest energy point. However, the general shape of the cross section in the higher energy region ($E \gtrsim 10^{-2}$ eV) is in good agreement. A complication of this system in contrast to the H_2^+ system arises from the fact that a single-electron, change-transfer channel, $He^+(1s)+He^+(1s)$, lies energetically below the RCT channels. The inelastic single charge transfer occurs predominantly through a radiative transition from $^1\Sigma_u^+$ to a single-electron charge-transfer state $^1\Sigma_g$ (Ref. 23), in this energy regime. An earlier calculation of the radiative charge-transfer cross section by Cohen and Bardsley[23] shows that the cross section increases monotonically as the energy is decreased, at least down to 10^{-3} eV. However, since the radiative charge-transfer cross section is not known for energies within the range of our interest, it is impossible to assess the influence of radiative charge transfer on the RCT process. We believe that since the largest contributions to the RCT cross section come from large impact parameters ($b \geq 15a_0$), whereas radiative charge transfer is more probable for small impact parameters ($R \lesssim 5a_0$), the RCT cross sections calculated here are not likely to be affected by the inclusion of the radiative charge transfer channel.

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