

Theoretical study of nonresonant ${}^3\text{He}^+ + {}^4\text{He} \rightleftharpoons {}^3\text{He} + {}^4\text{He}^+$ charge transfer in the threshold region

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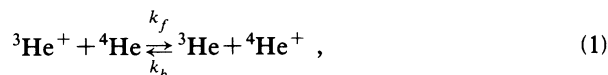
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(Received 18 September 1991; revised manuscript received 14 May 1992)

A quantum-mechanical calculation of charge-transfer cross sections for the forward (endothermic) and backward (exothermic) collision processes ${}^3\text{He}^+ + {}^4\text{He} \rightleftharpoons {}^3\text{He} + {}^4\text{He}^+$ in the threshold energy region has been carried out by using a two-state close-coupling treatment where the charge-transfer energy defect, approximately 1.3 meV, is the isotopic term difference between the ${}^3\text{He}$ and ${}^4\text{He}$ binding energies. The cross sections show numerous shape and orbiting resonances, which can be labeled with predissociation rotational and vibrational quantum numbers. From these cross sections, the forward and backward rate coefficients have been calculated. The present results, particularly the ratio of forward and backward rate coefficients, agree well with measurements of Schauer, Jefferts, and Dunn [Phys. Rev. A **42**, 5332 (1990)].

PACS number(s): 34.10.+x, 34.70.+e, 34.50.-s

Recently, measurements of the rate coefficients k_f and k_b for the forward (endothermic) and backward (exothermic) charge transfer processes,



were carried out by Schauer, Jefferts, and Dunn [1] at 8–80 K. Because of the different reduced electron masses for the two isotopes, the charge-transfer collision is slightly nonresonant, and the forward (backward) process is endothermic (exothermic) by approximately 1.3 meV (the difference in the binding energies of ${}^3\text{He}$ and ${}^4\text{He}$). Schauer, Jefferts, and Dunn [1] also estimated charge-transfer cross sections σ_b by using the Demkov model [2] and obtained an estimate of σ_f by using detailed balance. The dominant mechanism for the charge-transfer processes of Eq. (1) is resonant transfer. However, at very low velocities the effect of the reduced electron-nuclear mass, which removes the energy degeneracy in the asymptotic region, becomes important.

We have carried out quantum-mechanical calculations of σ_f and σ_b by using a two-state close-coupling treatment. Thorson and Delos [3] presented a rigorous approach based on the use of the molecular orbital (MO) representation in the inner region ($R < R_0$) and the modified atomic orbital (AO) representation in the outer region ($R > R_0$). They chose as the electronic basis functions, the linear combinations of molecular orbitals (LCMO) corresponding to the lowest ${}^2\Sigma_g$ and ${}^2\Sigma_u$ MO states in the outer R region, namely,

$$\phi_B(\mathbf{r}; R) = \frac{1}{\sqrt{2}} [\varphi_g(\mathbf{r}; R) + \varphi_u(\mathbf{r}; R)] \quad (2a)$$

and

$$\phi_A(\mathbf{r}; R) = \frac{1}{\sqrt{2}} [\varphi_g(\mathbf{r}; R) - \varphi_u(\mathbf{r}; R)], \quad (2b)$$

where φ_g and φ_u are eigenfunctions of the molecular electronic Hamiltonian, with gerade and ungerade symmetry, which correspond to the respective eigenvalues $\epsilon_g(R)$ and $\epsilon_u(R)$. In the asymptotic limit, $\phi_B(\mathbf{r}; R)$ and $\phi_A(\mathbf{r}; R)$ approach the atomic orbitals that represent an electron bound to nucleus B and A , respectively. [Note: $\phi_A(\mathbf{r}; R)$ and $\phi_B(\mathbf{r}; R)$ have *molecular* character at finite R and are equivalent to the respective AO *only* in the asymptotic region.] In their approach [3], a transformation between the MO and modified AO representations is carried out at an intermediate separation $R = R_0$. This method was applied by Davis and Thorson [4] in a detailed study of symmetric, resonant $\text{H}^+ + \text{H}$ and asymmetric, nonresonant $\text{H}^+ + \text{D}$ collisions below 0.1 eV. They chose R_0 to be the separation where the isotope splitting Δ and the potential difference between gerade and ungerade adiabatic potentials become comparable in magnitude.

In the present study of helium charge transfer, we have chosen an approach in which the modified AO representation Eqs. (2a) and (2b) is adopted at *all* internuclear separations. Since transformation between MO and modified AO representations is independent of R , the two approaches are formally equivalent. The total scattering wave function $\Psi(\mathbf{r}; \mathbf{R})$ is written in the two-state approximation as a superposition of products of the electronic functions, (2a) and (2b), and nuclear wave functions $F_A(\mathbf{R})$ and $F_B(\mathbf{R})$ in the form

$$\Psi(\mathbf{r}, \mathbf{R}) = \phi_B(\mathbf{r}, R) F_B(\mathbf{R}) + \phi_A(\mathbf{r}, R) F_A(\mathbf{R}). \quad (3)$$

Substitution of the total scattering wave function into the Schrödinger equation yields coupled equations for the nuclear wave function,

$$\left[-\frac{1}{2\mu} \nabla_R^2 + h + I - E \right] F(R) = 0, \quad (4)$$

where

$$h_{nm} = \left\langle \phi_n \left| h + \frac{4}{R} \right| \phi_m \right\rangle, \quad (5a)$$

$$I_{nm} = \left\langle \phi_n \left| -\frac{1}{2\mu} \nabla_R^2 \right| \phi_m \right\rangle, \quad (5b)$$

where $n, m = A$ and B . In Eq. (4), μ is the reduced nuclear mass 3135.24 a.u. and h and I are the electronic Hamiltonian and the isotope splitting operators, respectively, given in Eqs. (5). E is the total energy of the system, i.e., $E = k_B^2/2\mu + \varepsilon_B^0 = k_A^2/2\mu + \varepsilon_A^0$, where $k_B^2/2\mu$ and $k_A^2/2\mu$ are the respective kinetic energies of relative motion of the ion with respect to the neutral atom B and A , and ε_B^0 and ε_A^0 are the respective electronic energies.

The isotope splitting terms are approximated by their asymptotic values as

$$I_{nm} = \frac{-1}{2\mu} \langle \phi_n | \nabla_R^2 | \phi_m \rangle \cong [\varepsilon_n^0 - \varepsilon(\infty)] \delta_{mn}, \quad (6)$$

where $\varepsilon(\infty)$ is the asymptotic value of the degenerate molecular potential energies, viz., $\varepsilon(\infty) = \varepsilon_g(\infty) = \varepsilon_u(\infty)$. The asymptotic approximation used for determining the coupling matrix element should be very good since, as Davis and Thorson showed, the coupling is important only at large internuclear separations where the isotope splitting and the molecular potential energy splitting are comparable. (See Refs. [3] and [4] for details of the derivation.) Because He is more tightly bound relative to H, this approximation should be valid.

The electronic Hamiltonian matrices can be expressed using Eq. (2) as

$$\langle \phi_n | h | \phi_m \rangle = \begin{cases} \frac{1}{2} [\varepsilon_g(R) + \varepsilon_u(R)] & n = m \\ \frac{1}{2} [\varepsilon_g(R) - \varepsilon_u(R)] & n \neq m \end{cases}. \quad (7)$$

The two-state coupled equations for the (nuclear) scattering wave functions $F_A(R)$ and $F_B(R)$ are explicitly given by

$$\left\{ -\frac{1}{2\mu} \nabla^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} V_+ - \frac{k_B^2}{2\mu} & V_- \\ V_- & V_+ - \frac{k_A^2}{2\mu} \end{pmatrix} \right\} \begin{pmatrix} F_B(R) \\ F_A(R) \end{pmatrix} = 0, \quad (8)$$

where $V_{\pm} = \frac{1}{2} [V_g(R) \pm V_u(R)]$ and

$$\begin{aligned} V_g(R) &= \varepsilon_g(R) - \varepsilon(\infty), \\ V_u(R) &= \varepsilon_u(R) - \varepsilon(\infty). \end{aligned} \quad (9)$$

It is important to emphasize that Eqs. (8) do not contain any coupling resulting from the ∇_R^2 term in Eq. (5b). The

choice of the LCMO basis of Eqs. (2a) and (2b) causes the off-diagonal (coupling) terms in I to vanish as indicated in Eq. (6); the only approximation made here is to assume that the ∇_R^2 matrix elements may be replaced by their asymptotic values. Davis and Thorson made the same assumptions. With these assumptions, as discussed, these two approaches are formally equivalent.

For the potentials $V_g(R)$ and $V_u(R)$, we adopted the lowest $^2\Sigma_g^+$ and $^2\Sigma_u^+$ adiabatic potentials of He_2^+ given by Chen, Wang, and Watson [5] as shown in Fig. 1. These potentials have the form

$$V_u(R) \equiv \frac{\alpha_1}{R} e^{-\beta_1 R} - \alpha_2 R^2 e^{-\beta_2 R} \quad (10)$$

and

$$V_g(R) \equiv V_u(R) + \alpha_3 e^{-\beta_3 R},$$

where the parameters $\alpha_1 = 7.9989$, $\alpha_2 = 1.219$, $\alpha_3 = 9.55531$, $\beta_1 = 2.1696$, $\beta_2 = 1.565105$, and $\beta_3 = 1.253921$ were obtained to fit the *ab initio* configuration-interaction (CI) results [6]. Since at the ultra-low collision energies studied here, distant (large R) collisions are expected to be important, we have modified each of the adiabatic potentials by adding a polarization term, which we represent by

$$V_p(R) = -\frac{\alpha}{2R^4} \left\{ 1 - \exp \left[-\left(\frac{R}{R_x} \right)^6 \right] \right\}, \quad (11)$$

where $\alpha = 1.383$ a.u. is the dipole polarizability of He [7], and R_x is an adjustable cutoff parameter. The choice of R_x is somewhat arbitrary. However, we find (semiempirically) that values of R_x between 4.5 and 5.5 a.u. appear to be optimal. These R_x values seem rather large, given the tight electron distribution of He [8]. However, since Browne believes [9] that the adiabatic CI potentials [6]

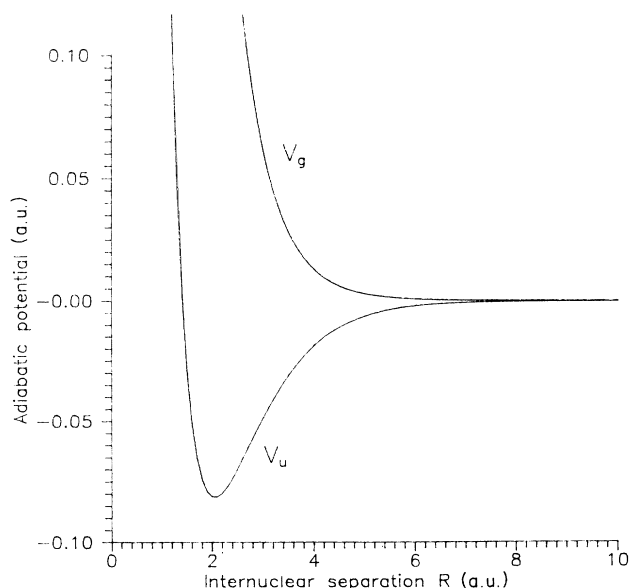


FIG. 1. Adiabatic potentials of He_2^+ system.

include some amount of polarization, at least at intermediate separations, we consider the large R_x values to be reasonable. Within this range of R_x , we selected three illustrative values for the calculations described below. Because of the attractive well in the $^2\Sigma_u$ potential, several predissociation rovibrational levels lead to shape and orbiting resonances in the cross sections at very low collision energies.

By solving Eq. (8) (by carrying the solution out to $100a_0$) we obtained the charge-transfer cross sections for the forward and backward processes, σ_f and σ_b , shown in Figs. 2(a) and 2(b). As expected, sharp resonance structures are apparent in σ_f and σ_b , particularly below collision velocity $v \sim 0.001$ a.u. The corresponding rovibrational levels (ν, J) are shown in Fig. 2. The dips in these cross sections around $v \sim 0.0003$ a.u. are caused by large destructive interferences among a small number of contributing partial waves that are scattered from the g and u potentials. (The dip was not present in the elastic-scattering cross sections.) The rather uniform oscillations above $v \sim 0.001$ a.u. are also due to interference between scattered waves in the g and u states. For energies well above the threshold, the charge-transfer S -matrix elements are proportional to $\sin[\eta_g^l - \eta_u^l]$, where η_g^l and η_u^l represent elastic phase shifts corresponding to the g and u potentials, respectively. Oscillations as a function of l do not wash out in the partial wave sum at low energies, resulting in coherent oscillations in the cross sections. For energies decreasing to the threshold value (~ 1.3 meV), σ_f drops sharply (vanishing at threshold), while σ_b increases. Since we only included energetically open channels in the calculations, we do not observe Feshbach resonances [4]. The cross sections at velocities less than ~ 0.0006 a.u. are found to be somewhat sensitive to the cutoff parameter R_x . The cross sections are also sensitive to variations in $V_g - V_u$. A truly *ab initio* treatment of this collision problem will require an accurate determination of the molecular potentials.

In Fig. 3 the theoretical forward and backward rate coefficients k_f and k_b for $R_x = 4.5, 5.0$, and 5.5 a.u., calculated by integrating the product of velocity v , $\sigma(v)$, and $f(v)$ from 0 to ∞ [where $f(v)$ is the Maxwell-Boltzmann velocity distribution] are compared with the measurements by Schauer *et al.* [1] for temperatures from 8 to 80 K. The rate coefficients are found to be sensitive to R_x at low temperatures below 40 K, although they rapidly converge above this temperature. The minimum in k_b at 10–20 K is the combined effect of the sharp increase of σ_b with decreasing velocity and the falloff of the Maxwell-Boltzmann function. For the exact resonant cases, $^3\text{He}^+ - ^3\text{He}$ or $^4\text{He}^+ - ^4\text{He}$, the resonant charge-transfer cross sections possess maxima in the very low energy region and remain nearly constant at much lower energies, as shown explicitly by us [10] for the $\text{H}^+ - \text{H}$ and $\text{He}^{2+} - \text{He}$.

In Fig. 4, we show the natural logarithm of the ratio k_b/k_f as a function of the inverse temperature. This plot is significant since in the case of the Boltzmann distribution, the slope of the curve is expected to yield the isotope energy splitting, i.e., 1.3 meV. Figure 4 shows that

the slope is rather insensitive to R_x , having the values 0.1302, 0.1304, and 0.1337 meV for $R_x = 4.5, 5.0$, and 5.5 a.u., respectively.

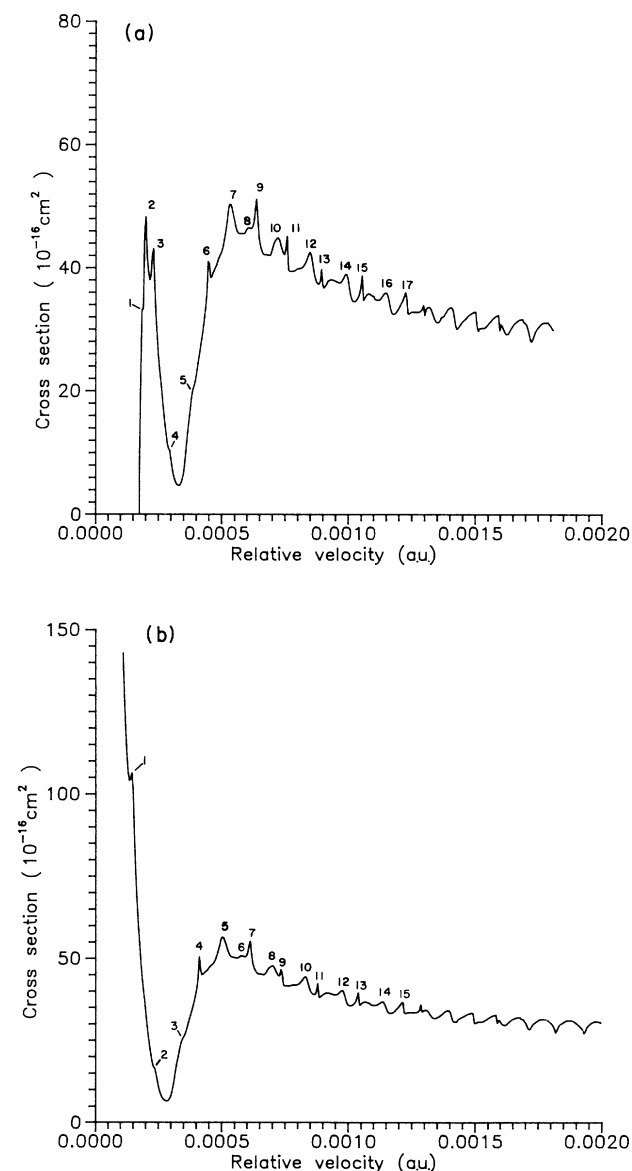


FIG. 2. Charge-transfer cross section for (a) forward and (b) backward processes with $R_x = 5.0$ a.u.. When R_x is varied between 4.5 and 5.5 a.u., the peak positions shift slightly. However, the features are essentially the same. Vibrational and rotational quantum numbers (ν, J) of the peaks are the following: In (a), (1) 22, 4; (2) 21, 6; (3) 20, 7; (4) 19, 11; (5) 19, 12; (6) 18, 15; (7) 18, 16; (8) 17, 17; (9) 17, 19; (10) 17, 20; (11) 16, 22; (12) 16, 23; (13) 15, 25; (14) 14, 26; (15) 14, 28; (16) 13, 29; (17) 13, 30. Among them, (4), (6), (9), (11), (14) and (15) are shape resonances, while the others are orbiting resonances. In (b), (1) 20, 7; (2) 19, 11; (3) 19, 12; (4) 18, 15; (5) 18, 16; (6) 17, 17; (7) 17, 19; (8) 17, 20; (9) 16, 22; (10) 16, 23; (11) 15, 25; (12) 14, 26; (13) 14, 28; (14) 13, 29; (15) 13, 30. Here (2), (4), (7), (9), (12), and (13) are shape resonances, while the others are orbiting resonances.

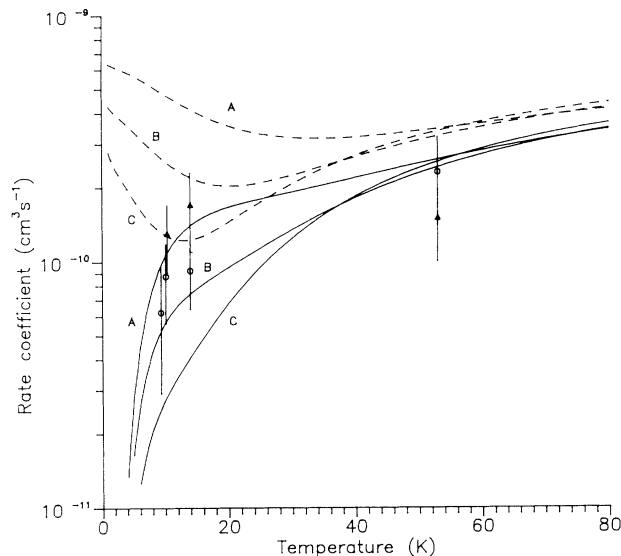


FIG. 3. Rate coefficients for k_f and k_b . Solid line, calculated k_f ; dashed line, calculated k_b ; ○, forward process, (experiment [1]); ▲, backward process (experiment [1]). The lines A, B, and C represent $R_x = 4.5, 5.0,$ and 5.5 a.u., respectively.

In summary, the present quantum-mechanical two-state, close-coupling calculations give rate coefficients k_f and k_b for the nonresonant charge-exchange processes discussed here that are in fairly good agreement with recent measurements. The calculated ratios k_b/k_f are in very good agreement with the measurements except at the lowest temperature measured.

This work was supported in part by the U.S. Department of Energy, Office of Energy Research, Office of Health and Environmental Research, under Contract No.

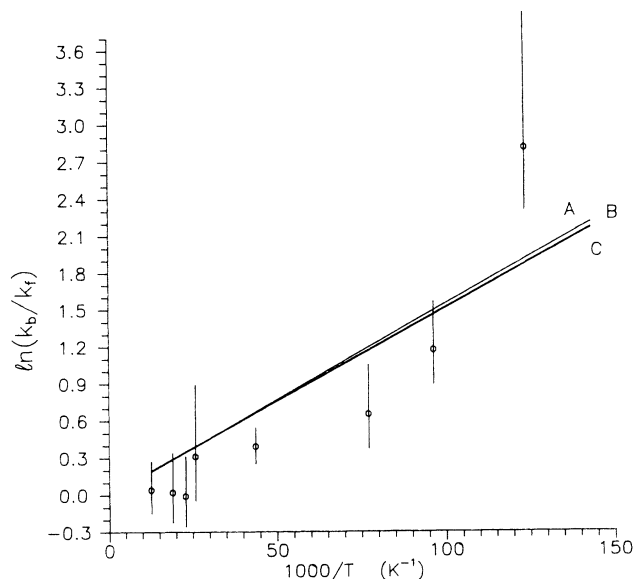


FIG. 4. van't Hoff plot, i.e., logarithm of ratio of k_b/k_f vs. inverse temperature. The lines A, B, and C represent $R_x = 4.5, 5.0,$ and 5.5 a.u., respectively. Symbols represent experimental values [1].

W-31-109-Eng-38 (M.K.), by the Office of Basic Energy Sciences, Division of Chemical Sciences; and by the Robert A. Welch Foundation (C.M.D. and N.F.L.). The computations were carried out at the National Energy Research Supercomputer Center facilities in Livermore. The authors appreciate having access to the experiments of Dr. G. H. Dunn and his colleagues prior to publication. One of the authors (C.M.D.) thanks Dr. W. R. Thorson for discussions concerning the approach used in Ref. [4]. We also thank Dr. N. Shimakura for providing a computer program for rovibrational level calculations.

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