Calculation of radiative single-charge-transfer cross sections for collisions of He^{2+} with He at low energy

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A theoretical study of low-energy collisions of He^{2+} with He has been made. Potential curves are obtained using generalized valence-bond wave functions for the $X\,^1\Sigma_g^+$ state formed from $He^+ + He^+$ and the $B\,^1\Sigma_u^+$ and $E\,^1\Sigma_g^+$ states formed from $He^{2+} + He$. The predominant mechanism for single charge transfer is a radiative transition. The dipole transition moment connecting the B and X states is calculated using the *ab initio* wave functions. The radiative collision problem is formulated in terms of a complex potential and solved in the JWKB approximation. Cross sections are presented for energies from 0.001 to 10 eV. A rate constant of 3.6×10^{-14} cm^3/sec at 300 K is obtained. This value is in satisfactory agreement with the recent experimental result and there is some evidence that the remaining discrepancy is due to the effect of tunneling and shape resonances, which have been estimated to increase the rate to 4.4×10^{-14} cm^3/sec. The splitting of the asymptotically degenerate $B\,^1\Sigma_u^+$ and $E\,^1\Sigma_g^+$ states is also examined and a conflict with a recent prediction of the asymptotic splitting is resolved.

I. INTRODUCTION

Drift-tube experiments have been conducted recently to study low-energy collisions between He^{2+} ions and He atoms.[1] In order to provide theoretical analyses of these experiments one needs to determine the molecular interactions of He_2^{2+}. Potential curves for the appropriate states of this molecular ion were recently computed by Yagisawa *et al.*[2] using wave functions with up to 75 configurations of the James-Coolidge type. However, the basis set employed in that study does not permit the exact representation of two He^+ ions at infinite separation and appears to give a poor approximation to the asymptotic limit of $He + He^{2+}$. On the other hand, the valence-bond calculations by Browne[3] led to good results at large internuclear distances but to less accurate results at small separations.

The variational calculations have been challenged by Chibisov,[4] following his analysis of the interaction between He^{2+} ions and ground-state He atoms. Chibisov calculates the potential energy difference between the $^1\Sigma_g^+$ and $^1\Sigma_u^+$ states that dissociate to this limit and argues that the $^1\Sigma_g^+$ energy should be the lower. This result is inconsistent with the calculations of both Yagisawa *et al.*[2] and Browne.[3]

In this paper we report extended calculations based on the method of Browne (generalized valence bond) that provide potential curves which are accurate at intermediate to large R, and thus complement the results reported by Yagisawa *et al.* We also argue that Chibisov's analysis is incorrect. We present results on the $^1\Sigma_g^+$ and $^1\Sigma_u^+$ states which dissociate to ground-state He plus He^{2+} and the lower $^1\Sigma_g^+$ state which dissociates to two He^+ ions. Our attention has been concentrated on nuclear separations greater than $2.0a_0$, which are accessible in low-energy collisions of He^{2+} with He.

The present calculations confirm that no potential curve crossings or avoided crossings are important in thermal collisions. Although resonant double charge transfer occurs readily, owing to the interference between the $(^1\Sigma_g^+)^*$ and $^1\Sigma_u^+$ states, the inelastic single charge transfer occurs predominantly through a radiative transition from the $^1\Sigma_u^+$ to the $^1\Sigma_g^+$ ground state. The probability of such transitions is calculated and the cross section for radiative charge transfer is estimated by the JWKB method using a complex potential.

II. METHOD

The basis set employed by Browne was comprised mostly of Slater-type orbitals (STO's). The orbitals and exponents were $1s$ (1.97), $2s$ (2.09), $3s$ (2.18), $2p(\sigma,\pi)$ (2.93), $3p(\sigma,\pi)$ (2.93), and $3d(\sigma,\pi,\delta)$ (3.61). In order to improve the description of the polarization of the He atom, four elliptical orbitals were introduced of the form

$$\phi_i^{\pm}(\vec{r}) = \exp\left[-\frac{\alpha_i}{R}(r_a+r_b) \mp \frac{\beta_i}{R}(r_a-r_b)\right], \quad i=1,2, \tag{1}$$

where r_a and r_b are the distances of the electron from nuclei a and b, respectively. The elliptical orbital exponents were reoptimized at each internuclear distance with respect to the $^1\Sigma_u^+$ energy; the same exponents were found to be near optimum for the two $^1\Sigma_g^+$ states.

The trial wave function was initially constructed

as a linear combination of all possible products of two STO's consistent with the overall symmetry ($^1\Sigma_g^+$ or $^1\Sigma_u^+$) together with two terms containing the elliptical orbitals. The spatial portion of the latter two terms can be written

$$\psi^{\pm}(\vec{r}_1,\vec{r}_2)=(1+P_{12})[\phi_1^+(\vec{r}_1)\phi_2^{\pm}(\vec{r}_2)+\lambda\phi_1^-(\vec{r}_1)\phi_2^{\mp}(\vec{r}_2)]\,, \tag{2}$$

where P_{12} is the permutation operator for electrons 1 and 2, and $\lambda=+1$ for $^1\Sigma_g^+$ and -1 for $^1\Sigma_u^+$.

Although our primary interest is in the region of nuclear separations greater than $2a_0$, we performed exploratory calculations to $R=1a_0$. For $R\lesssim 1.5a_0$ the above wave function yields relatively poor results for the excited $^1\Sigma_g^+$ state. The calculations of Yagisawa *et al.*[2] show an avoided crossing near 1.3 eV with a state that dissociates to $He^+(1s)+He^+(2s$ or $2p)$. We therefore added terms of this type, with a relatively diffuse $2s'$ or $2p'$ orbital. Only the addition of the $2s'$ orbital resulted in a significant lowering of the energy. This orbital with exponent 1.24 was thus added to the basis set at all separations and included in configurations $1s2s'$ and $2s2s'$. The complete wave function contained 60 terms for the $^1\Sigma_g^+$ states and 50 terms for the $^1\Sigma_u^+$ state, the different numbers arising because $^1\Sigma_u^+$ configurations cannot be formed using the same orbital on both nuclei.

Having obtained the wave functions ψ_g and ψ_u for the $^1\Sigma_g^+$ and $^1\Sigma_u^+$ states, with energies E_g and E_u, the dipole transition matrix element was computed using both the length and velocity formulations,

$$\vec{\mu}_l(R)=\langle\psi_u|\vec{r}_1+\vec{r}_2|\psi_g\rangle \tag{3}$$

and

$$\vec{\mu}_v(R)=[\Delta E(R)]^{-1}\langle\psi_u|(1/i)(\vec{\nabla}_1+\vec{\nabla}_2)|\psi_g\rangle \tag{4}$$

(in atomic units), respectively, where

$$\Delta E(R)\equiv E_u(R)-E_g(R)\,.$$

The transition rate at fixed R is given by the Einstein A coefficient

$$A(R)=\tfrac{4}{3}(g/c^3)[\Delta E(R)]^3|\vec{\mu}(R)|^2\,, \tag{5}$$

where g is the degeneracy of the final state (unity here) and c is the velocity of light.

The radiative decay of the $^1\Sigma_u^+$ state can be described quantum mechanically by adding an imaginary part to the potential. The resulting complex potential is expressed as

$$W(R)=V(R)-\tfrac{1}{2}i\hbar A(R)\,. \tag{6}$$

Scattering by this potential leads to a complex phase shift

$$\eta_l=\eta_l^R+i\,\eta_l^I\,. \tag{7}$$

The cross section for photon emission is then given by

$$\sigma(E)=\frac{\pi}{k^2}\sum_l(2l+1)(1-e^{-4\eta_l^I})\,, \tag{8}$$

in which k is the wave number corresponding to the relative motion of the nuclei. For collisions of identical spin-zero particles (such as ^4He), only even l contribute to g-state scattering and only odd l contribute to u-state scattering.

Cohen and Lane[5] have shown that under conditions where barrier penetration is unimportant, the JWKB approximation leads to accurate estimates of the emission cross sections. The JWKB technique is used here, and in a future paper we will examine the effects of shape resonances that arise from tunneling through the centrifugal barrier.

III. POTENTIAL CURVES

Our calculated potential energies for the three lowest states of He_2^{2+} are given in Table I and Fig. 1. Our basis set permits an essentially exact represenation of the asymptotic limit for the ground state. For the states which dissociate to $He^{2+}+He$, our asymptotic limit is $-2.901\,50$ a.u., which is $0.002\,22$ a.u. above the exact value (in the fixed-nuclei approximation). For $R\gtrsim 2.5a_0$ our $^1\Sigma_g^+$ curves lie below those obtained by Yagisawa *et al.*,[2] and for the $^1\Sigma_u^+$ state our curve is lower for $R\gtrsim 3a_0$. We estimate that for $R\gtrsim 2a_0$ the absolute error in our energies should be less

TABLE I. Potential energies (total) for He_2^{2+}.

R (a_0)	E (a.u.) $X\,^1\Sigma_g^+$	$E\,^1\Sigma_g^+$	$B\,^1\Sigma_u^+$
1.0	-3.597 02	-1.284 90	-1.858 96
1.2	-3.670 56	-1.552 19	-2.250 00
1.3	-3.678 84	-1.647 55	-2.387 07
1.5	-3.670 62	-2.025 79	-2.584 23
1.75	-3.646 61	-2.401 07	-2.734 97
2.0	-3.629 37	-2.633 21	-2.821 68
2.25	-3.626 77	-2.770 10	-2.870 57
2.5	-3.637 29	-2.845 84	-2.897 02
2.75	-3.655 58	-2.884 85	-2.910 24
3.0	-3.676 74	-2.903 56	-2.915 93
3.25	-3.697 85	-2.911 32	-2.917 37
3.5	-3.717 55	-2.913 66	-2.916 64
4.0	-3.751 41	-2.912 23	-2.912 98
4.5	-3.778 54	-2.909 15	-2.909 34
5.0	-3.800 48	-2.906 56	-2.906 64
6.0	-3.833 55	-2.903 76	-2.903 78
8.0	-3.875 07	-2.902 16	-2.902 16
10.0	-3.900 03	-2.901 75	-2.901 75
∞	-4.000 00	-2.901 50	-2.901 50

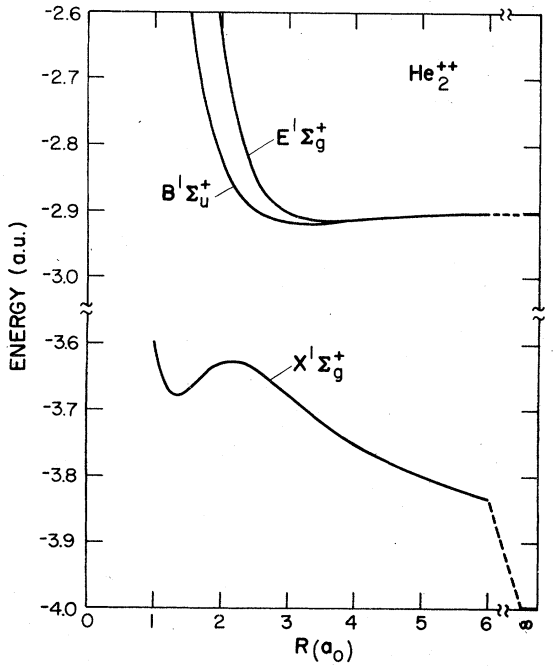

FIG. 1. Calculated He_2^{2+} potential-energy curves for He^+ (^2S) + He^+ (^2S) and He^{2+} + He (^1S) interactions.

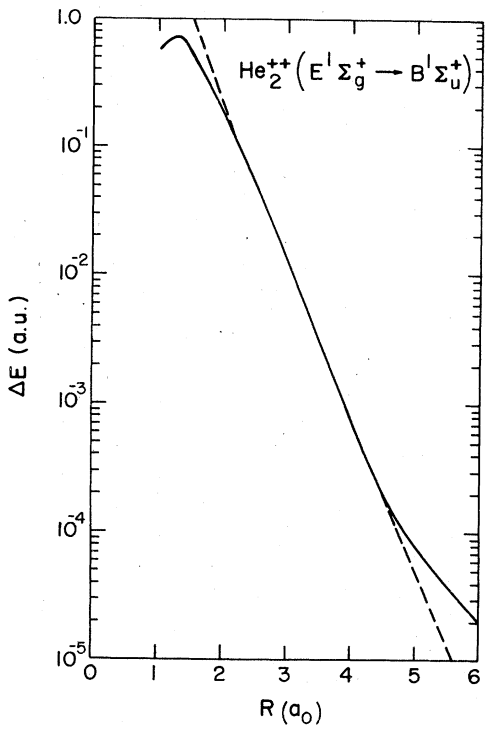

FIG. 2. Potential-energy difference between the $E^1\Sigma_g^+$ and $B^1\Sigma_u^+$ states which arise from the interaction of He^{2+} with the ground-state He atom. Solid curve is *ab initio* calculation. Dashed curve is asymptotic fit given by Eq. (11).

than 0.1 eV, and that the relative error between two points on the same curve should be significantly smaller.

The minima in the $^1\Sigma_u^+$ and $(^1\Sigma_g^+)^*$ potentials occur at $R \simeq 3.3a_0$ and $3.5a_0$, respectively, with well depths of about 0.44 and 0.33 eV. For thermal collisions with zero angular momentum the classical turning points are near $2.6a_0$ for the $^1\Sigma_u^+$ state and $3.0a_0$ for the $(^1\Sigma_g^+)^*$ state. In the asymptotic region our calculations reproduce over 90% of the expected polarization interaction, and for R around $5a_0$ show a significant contribution arising from the higher-order electrostatic interactions.

By examination of the effects of double charge transfer Chibisov[4] predicts the asymptotic splitting between the $(^1\Sigma_g^+)^*$ and $^1\Sigma_u^+$ curves to be

$$\Delta E(R) \equiv E_g(R) - E_u(R)$$
$$\simeq -52.7R^{-0.537}e^{-2.688R} - 35.4R^{0.962}e^{-3.344R}. \quad (9)$$

Earlier, Komarov and Yanev[6] had obtained the result

$$\Delta E(R) = CR^{2.463}e^{-2.688R}, \quad (10)$$

in which C is a positive constant. These two results differ in sign and in the R dependence. Our calculations agree with Chibisov's prediction with respect to the shape and order of magnitude of $\Delta E(R)$ but differ in sign. His analysis of the effects of double electron exchange seems to be essentially correct, but he has neglected to allow for the orthogonalization of the $(^1\Sigma_g^+)^*$ state to the ground state. A simple analysis with single-configuration wave functions suggests that this effect should have a similar R dependence to the first term in Eq. (9). Thus our computed energy differences can be fit by the expression

$$\Delta E(R) = AR^{-0.537}e^{-2.688R} - 35.4R^{0.962}e^{-3.344R}, \quad (11)$$

with $A = 95$. The fit, as shown in Fig. 2, is good in the region $2.5a_0 \leq R \leq 4.5a_0$. At larger R, where ΔE is quite small, the disagreement is presumably due to inaccuracies in the computed values, whereas at smaller R a simple asymptotic analysis is not applicable. We have performed quantum-mechanical calculations of cross sections for double charge transfer using the new potential curves (see following paper).

IV. RADIATIVE CHARGE TRANSFER

The dipole transition matrix elements connecting the $^1\Sigma_u^+$ and ground $^1\Sigma_g^+$ states, calculated

TABLE II. Dipole transition moments calculated in the length and velocity formulations for the $B\,^1\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+$ transition in He_2^{2+}. The energy ΔE and Einstein A coefficient are also given.

$R\ (a_0)$	μ_l (a.u.)[a]	μ_v (a.u.)[a]	ΔE (a.u.)	A (a.u.)
1.0	0.726 22	0.726 95	1.738 05	1.43×10^{-6}
1.2	0.806 55	0.806 85	1.420 55	9.66×10^{-7}
1.3	0.839 58	0.839 62	1.291 77	7.87×10^{-7}
1.5	0.889 24	0.888 41	1.086 39	5.25×10^{-7}
1.75	0.911 09	0.910 38	0.911 64	3.26×10^{-7}
2.0	0.878 32	0.877 90	0.807 69	2.11×10^{-7}
2.25	0.791 88	0.791 84	0.756 20	1.40×10^{-7}
2.5	0.672 26	0.672 25	0.740 27	9.50×10^{-8}
2.75	0.546 81	0.546 84	0.745 34	6.41×10^{-8}
3.0	0.433 82	0.433 89	0.760 80	4.29×10^{-8}
3.25	0.339 23	0.339 26	0.780 48	2.83×10^{-8}
3.5	0.263 08	0.263 11	0.800 90	1.84×10^{-8}
4.0	0.155 69	0.155 73	0.838 43	7.40×10^{-9}
4.5	0.090 45	0.090 49	0.869 21	2.78×10^{-9}
5.0	0.051 79	0.051 89	0.893 84	9.92×10^{-10}
6.0	0.016 16	0.016 20	0.929 78	1.09×10^{-10}
8.0	0.001 37	0.001 37	0.972 91	8.96×10^{-13}
10.0	0.000 08	0.000 08	0.998 28	3.76×10^{-15}

[a] 1 a.u. (electric dipole moment) = 2.542 D.

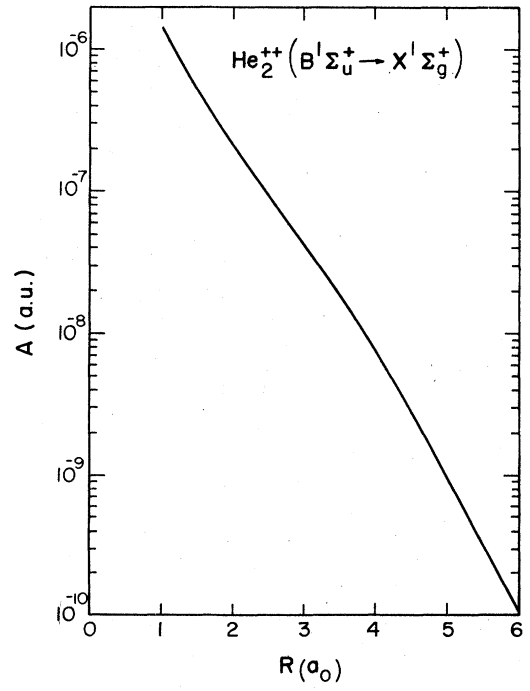

FIG. 3. Einstein A coefficient (R dependent) for transitions from the $B^1\Sigma_u^+$ to the $X^1\Sigma_g^+$ state of He_2^{2+}.

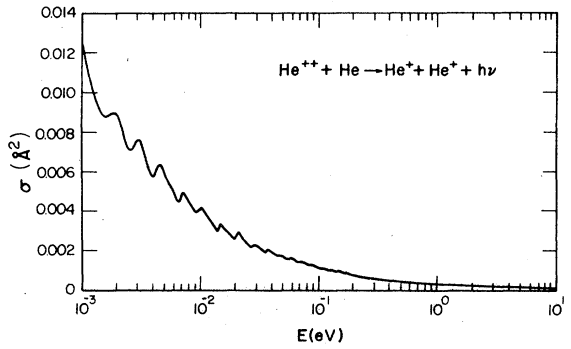

FIG. 4. Cross section for radiative single charge transfer in collisions of He^{2+} with He as a function of relative energy.

by Eqs. (3) and (4), are listed in Table II. The results in the length and velocity formulations agree to three significant figures. The Einstein A coefficient for the $B^1\Sigma_u^+ - X^1\Sigma_g^+$ transition, calculated by Eq. (5), is shown in Fig. 3. The real part of the complex potential, Eq. (6), is provided by the potential energy curve of the $^1\Sigma_u^+$ state. The real potential was cubic spline fit for $R \leq 8a_0$ and extrapolated to larger R by the polarization potential $-2.766/R^4$. The Einstein A coefficient was cubic spline fit for $R \leq 6a_0$ and extrapolated to larger R by the form $(1.95\times10^{-4})\exp(-2.4R)$. The corresponding complex partial wave phase shifts were evaluated in the JWKB approximation using a very fast and accurate quadrature scheme recently suggested.[7] With the nuclear spin statistics taken into account the sum over partial waves in Eq. (8) includes only odd l.

The resulting cross section for single charge transfer accompanied by radiation is shown in Fig. 4 as a function of collision energy (in the center-of-mass system). The structure at low energies is due to the discrete sum over partial waves. For collision energies $E \lesssim 0.2$ eV, the centrifugal barrier tends to abruptly cut off the partial wave contributions. In a fully quantum-mechanical treatment, which will be pursued in future work, one may expect that the cross section at these energies will be increased by the contributions of shape resonances associated with the centrifugal barriers.

Using the cross section of Fig. 4, rate constants

$$K = \overline{v\sigma} \tag{12}$$

for Maxwellian velocity distributions at various temperatures are obtained. The temperature dependence of the rate constant is weak, its value decreasing by only about 15% as the temperature is increased from 100 to 10 000 K. The theoretical rate constant at 300 K, $K = 3.6\times10^{-14}$ cm^3/sec,

should be compared with the value $4.8 \pm 0.5 \times 10^{-14}$ cm^3/sec recently obtained experimentally by Johnsen and Biondi.[1] An earlier theoretical determination by Allison and Dalgarno[8] yielded a rate constant an order of magnitude smaller than our value with an opposite temperature dependence. The main reason for this difference is that their dipole transition moment is only about 40% as large as ours at the maximum ($R \simeq 2a_0$) and falls off more rapidly at larger R. The smaller transition moment apparently resulted from neglect of polarization in the wave function used to calculate the matrix element.

The major deficiency of the present JWKB approximation is that it underestimates the effect of tunneling into classically forbidden regions and makes no allowance for the existence of shape resonances. Quantum calculations are underway to determine the importance of these effects, but in the meantime the contribution of resonances has been estimated using the method described by Bain and Bardsley.[9] The $^1\Sigma_u^+$ potential supports approximately 15 vibrational levels with zero angular momentum ($J=0$). As J is increased the levels are pushed up into the continuum and no bound states remain at $J=37$. We have estimated the energies and radiative decay rates of the resonant states by extrapolating the bound-state properties as a function of J, and have estimated the predissociation rates by a semiclassical calculation of the barrier penetration probability. The results imply that the vibrational levels between $v=2$ and $v=9$ lead to significant resonances with J between 13 and 35, and that the total contribution from the resonances to the radiative charge transfer rate is about 8×10^{-15} cm^3/sec, resulting in a total theoretical rate of 4.4×10^{-14} cm^3/sec, in excellent agreement with experiment. This suggests that much, if not all, of the discrepancy between the semiclassical calculation and experiment can be attributed to the effects of tunneling.

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