Direct charge transfer of He^+ in neon

B. Zygelman and A. Dalgarno
Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138
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The cross sections for direct charge transfer of He^+ ions in low-energy collisions with neon atoms are calculated in a diabatic formulation for several choices of the origin of coordinates. It is shown numerically that the omission of electronic translation factors creates serious uncertainties at intermediate energies. The differences in the cross sections diminish as the collision energies increase to 900 eV where they attain a value of 1×10^{-16} cm^2. Direct charge transfer is more efficient than radiative charge transfer at energies above about 25 eV.

I. INTRODUCTION

At thermal energies, the direct charge transfer

$$He^+ + Ne \rightarrow He + Ne^+ \tag{1}$$

of He^+ ions in collisions with neon atoms is negligibly slow and He^+ ions traversing a gas of neon are removed by radiative charge transfer[1,2]

$$He^+ + Ne \rightarrow He + Ne^+ + h\nu\,, \tag{2}$$

and by radiative association

$$He^+ + Ne \rightarrow HeNe^+ + h\nu\,. \tag{3}$$

With increasing velocity, reaction (1) becomes more probable and above some impact energy it is more rapid than the radiative processes.

All three processes can be regarded as transitions from the $B\,^2\Sigma^+$ state of the molecular ion $HeNe^+$ to the $A\,^2\Pi$ and $X\,^2\Sigma^+$ states. In (1), the transitions are induced by the motion of the nuclei and in (2) and (3) by the interaction with the radiation field.

II. THEORY

We ignore the rotational coupling of the $B\,^2\Sigma^+$ and $A\,^2\Pi$ states and we assume that at low energies direct charge transfer is driven by the radial component of the nuclear energy operator which couples the $B\,^2\Sigma^+$ and $X\,^2\Sigma^+$ electronic states. The matrix element $\langle\phi(B\,^2\Sigma^+)\,|\,(d/dR)\,|\,\phi(X\,^2\Sigma^+)\rangle$, where the ϕ's are electronic eigenfunctions, R is the internuclear distance, and the derivative is taken with the center of mass of the nuclei as origin, has been calculated by Barat *et al.*[3] who represent it by the formula

$$A_{12}(R)=\langle B\,^2\Sigma^+\,|\,(d/dR)\,|\,X\,^2\Sigma^+\rangle=\frac{0.56}{e^x+e^{-x}}\,, \tag{4}$$

where $x=1.12\ (R-3.9)$ and all quantities are measured in atomic units. Values of $A_{12}(R)$ for another coordinate origin O' on the nuclear axis may be obtained from the identity[4]

$$A'_{12}(R)=A_{12}(R)+\frac{\eta' M_2+(\eta'-1)M_1}{M_1+M_2}D_{12}(R)[\epsilon_2(R)-\epsilon_1(R)]\,, \tag{5}$$

where M_1 is the mass of the helium nucleus, M_2 is the mass of the neon nucleus, O' is located at a distance η' from the neon nucleus, $\epsilon_1(R)$ and $\epsilon_2(R)$ are, respectively, the adiabatic potential energy curves of the $B\,^2\Sigma^+$ and $X\,^2\Sigma^+$ states, and $D_{12}(R)$ is the electric dipole transition moment between them.

To represent the potential energy curves we adopted the Rydberg-Klein-Rees values[2,5,6] slightly modified at short distance to the forms

$$\begin{aligned}\epsilon_1(R)&=\frac{20}{R}\exp(-1.497R)-0.00748\,,\\ \epsilon_2(R)&=\frac{20}{R}\exp(-2.067R)-0.22166\end{aligned} \tag{6}$$

and extrapolated to large distances by the forms

$$\begin{aligned}\epsilon_1(R)&=\frac{-1.332}{R^4}\,,\\ \epsilon_2(R)&=\frac{-0.692}{R^4}-0.111\,.\end{aligned} \tag{7}$$

Values of $D_{12}(R)$ have been calculated by Cooper *et al.*[2] The coupling matrix elements $A'_{12}(R)$ corresponding to origins at the center of mass of the nuclei and at each nucleus, obtained by the use of Eq. (5), are reproduced in Fig. 1. There are considerable differences between the three functions so that the omission of electronic translations factors may introduce serious uncertainties into the calculated cross sections.

Because the relative sign of the calculated values of $A_{12}(R)$ and $D_{12}(R)$ is unknown, we cannot be sure that we have combined them correctly in Eq. (5). Without knowing the correct relative sign, we can use Eq. (5) only to make predictions on the value of $A'_{12}(R)$ at an absolute distance $|\eta-\eta'|$ from the center of mass on the internuclear axis. We arbitrarily choose $A_{12}(R)$ and $D_{12}(R)$ to have opposite signs so that the choices $\eta'=1,0$ in (5)

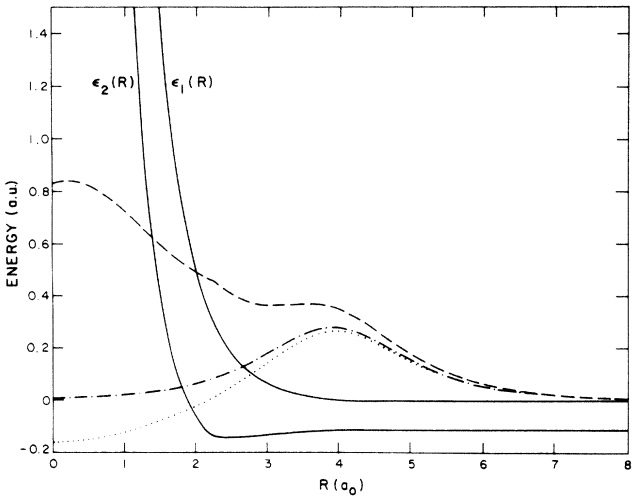

FIG. 1. The adiabatic potentials $\epsilon_1(R)$ and $\epsilon_2(R)$ and adiabatic coupling elements $A_{12}(R)$ corresponding to the origin at the center of mass (—·—·—·), the neon nucleus (· · · ·), and the helium nucleus (— — —).

predict the radial coupling when the electronic origin is placed on the helium and neon nuclei, respectively. In Table I we present the calculated cross sections for charge transfer for the choice of electronic origin at the helium and neon nuclei and at the center of mass; and in addition, in parentheses, the calculated cross sections when the origin is placed at points which are the nuclear origins, mirror-reflected on the internuclear axis with respect to the center of mass. These points correspond to the values $\eta=(M_1-M_2)/(M_1+M_2)$, and $\eta=2M_1/(M_1+M_2)$, for the helium and neon mirror-reflected origins, respectively. A change in the relative phase of A_{12},D_{12} would interchange the nuclear origin with its mirror-reflected value. The trend in Table I suggests that the qualitative features of the origin dependence of the cross sections is independent of the relative phase between A_{12} and D_{12}.

The cross section for direct charge transfer (1) at an incident energy E_1 of relative motion is given by

$$\sigma_{12}(E_1)=\frac{\pi}{2\mu E_1}\sum_J (2J+1)\,|\,S_{12}^J\,|^2\,, \tag{8}$$

where J is the orbital angular momentum of the nuclear motion and S_{12}^J is the off-diagonal element of the scattering matrix. The kinetic energy E_2 of the final state is related to E_1 by the conservation of energy

$$E=E_1+\epsilon_1(\infty)=E_2+\epsilon_2(\infty)\,. \tag{9}$$

The scattering matrix is obtained from the asymptotic solutions of the coupled equations of motion in channels 1 and 2 written in matrix form as

$$\left[\frac{-1}{2\mu}\left(\frac{d^2}{dR^2}-\frac{J(J+1)}{R^2}\right)+(\underline{\epsilon}-E\underline{I})-\frac{1}{2\mu}\left(2\underline{A}\frac{d}{dR}+\underline{B}\right)\right]\underline{g}^J=0\,, \tag{10}$$

where $\underline{g}^J$ is a square matrix with elements g_{ij}^J, $\underline{A}$ is a skew matrix with elements $A_{ij}=\langle\phi_i\,|\,(d/dR)\,|\,\phi_j\rangle$, $\underline{\epsilon}(R)$ is a diagonal matrix whose elements are the adiabatic potential energy curves $\epsilon_i(R)$, and $\underline{B}$ is a square matrix with elements $B_{ij}=\langle\phi_i\,|\,(d^2/dR^2)\,|\,\phi_j\rangle$.

It is convenient to transfer to a diabatic basis by writing[7,8]

$$\underline{g}=\underline{C}\underline{f}\,, \tag{11}$$

where $\underline{C}$ is a unitary matrix whose elements obey the differential equation

$$\frac{dC_{ij}}{dR}+\sum_k A_{ik}C_{kj}=0\,. \tag{12}$$

TABLE I. Cross sections for $He^+ + Ne \rightarrow He + Ne^+$ corresponding to different coordinate origins in units of 10^{-20} cm^2. Values in parentheses are cross sections when the origin is at the mirror-reflected position on the internuclear axis.

Energy (eV)	Helium	Center of mass	Neon
0.27	9.0×10^{-4} (8.2×10^{-4})	7.5×10^{-4}	7.4×10^{-4} (7.6×10^{-4})
2.72	2.4×10^{-3} (1.4×10^{-3})	1.3×10^{-3}	1.2×10^{-3} (1.4×10^{-3})
8.16	0.045 (0.031)	0.0046	0.0028 (0.015)
13.6	0.24 (0.089)	0.018	0.008 (0.040)
21.8	0.25 (0.107)	0.042	0.033 (0.068)
27.2	0.308 (0.109)	0.09	0.075 (0.115)
40.8	0.94 (0.22)	0.420	0.36 (0.503)
54.4	2.54 (1.10)	1.62	1.49 (1.77)
68.0	5.45 (3.98)	4.56	4.41 (4.71)
81.6	1.18×10 (9.26)	1.03×10	1.01×10 (1.06×10)
95.2	2.05×10 (2.07×10)	2.01×10	2.01×10 (2.01×10)
109	3.18×10 (3.93×10)	3.49×10	3.57×10 (3.41×10)
200	2.75×10^2 (3.53×10^2)	3.10×10^2	3.18×10^2 (3.02×10^2)
400	1.83×10^3 (2.39×10^3)	2.11×10^3	2.17×10^3 (2.06×10^3)
900	1.04×10^4 (9.88×10^3)	1.01×10^4	1.01×10^4 (1.02×10^4)
2000	3.72×10^4 (2.66×10^4)	3.14×10^4	3.04×10^4 (3.26×10^4)
4000	7.39×10^4 (4.50×10^4)	6.0×10^4	5.65×10^4 (6.26×10^4)
8000	9.49×10^4 (5.38×10^4)	7.64×10^4	7.18×10^4 (8.08×10^4)

Then

$$\left\{\frac{-1}{2\mu}\left[\frac{d^2}{dR^2}-\frac{J(J+1)}{R^2}\right]+(\underline{V}-E\underline{I})-\frac{1}{2\mu}\left[\underline{C}^{-1}\left[-\underline{A}^2-\frac{d\underline{A}}{dR}+\underline{B}\right]\underline{C}\right]\right\}\underline{f}^J=0\,, \quad (13)$$

where

$$\underline{V}=\underline{C}^{-1}\underline{\epsilon}\,\underline{C} \quad (14)$$

is the diabatic matrix. We may use the identity

$$B_{ij}=\sum_k A_{ik}A_{kj}+\frac{dA_{ij}}{dR}, \quad (15)$$

in which the summation is over the complete set of states k, to write the equation in the alternative form

$$\left\{\frac{-1}{2\mu}\left[\frac{d^2}{dR^2}-\frac{J(J+1)}{R^2}\right]+(\underline{V}-E\underline{I})+\frac{1}{2\mu}\left[\underline{C}^{-1}\left[\sum_{k\neq i,j}A_{ik}A_{kj}\right]\underline{C}\right]\right\}\underline{f}^J=0\,. \quad (16)$$

We now assume that off-diagonal coupling terms A_{ik} between states 1 and 2 and any other state of the $HeNe^+$ system are small at the nuclear separations sampled by the collisions. The scattering equations reduce to the pair of coupled equations

$$\left[\frac{-1}{2\mu}\left[\frac{d^2}{dR^2}-\frac{J(J+1)}{R^2}\right]+(V_{11}-E)\right]f_1^J+V_{12}f_2^J=0\,, \quad (17)$$

$$\left[\frac{-1}{2\mu}\left[\frac{d^2}{dR^2}-\frac{J(J+1)}{R^2}\right]+(V_{22}-E)\right]f_2^J+V_{21}f_1^J=0\,. \quad (18)$$

Avoided crossings of the $B\,^2\Sigma^+$ state with the $C\,^2\Sigma^+$ and $C'\,^2\Sigma^+$ state at, respectively, $1.86a_0$ and $1.77a_0$ have been predicted by Sidis and Lefebvre.[9] Experimental data[10] on the elastic scattering of He^+ by Ne at a collision energy of 40 eV are satisfactorily explained by the coupling of the elastic $B\,^2\Sigma^+$ channel with the excited direct $C\,^2\Sigma^+$ channel, suggesting that the influence of the $B\,^2\Sigma^+$–$C'\,^2\Sigma^+$ coupling is small. We assume that the coupling similarly has no effect on the $X\,^2\Sigma^+$–$B\,^2\Sigma^+$ charge transfer transition. We also ignore the $B\,^2\Sigma^+$–$C\,^2\Sigma^+$ coupling so that our calculations do not permit any of the charge transfer flux to enter the channel separating to He and an excited state of Ne^+. Nevertheless, our results for the total charge transfer of He^+ ions in neon should be reliable within the uncertainties created by the origin dependence of the nuclear momentum operators.

III. RESULTS

The elements V_{11}, V_{22}, and V_{12} of the diabatic potential matrix $\underline{V}(R)$ are illustrated in Figs. 2(a)–2(d) for the cases in which the coordinate origin is located at the helium nucleus, the center of mass, the neon nucleus, and at the point $\eta=(M_1-M_2)/(M_1+M_2)$. The choice of coordinate origin has a substantial effect on the magnitudes and variation with R of the potential matrix elements.

The coupled equations for the scattering wave function $\underline{f}^J(R)$ corresponding to the diabatic potentials were solved numerically using the log-derivative method of Johnson.[11] The resulting charge transfer cross sections are presented in Table I for energies of relative motion up to 8 keV.

The omission of translation factors is a serious defect at high energies.[12] Here we find, in a situation in which the coupling persists over an extended range of internuclear distances, that it also creates large uncertainties at intermediate energies. We may distinguish between three distinct regions of relative collision energy E. At low energies E less than approximately 3 eV, the cross sections are almost independent of the choice of coordinate origin. We show in Fig. 3(a) the transition probability $|S_{12}^J|^2$ at a collision energy of 1.36 eV as a function of the orbital angular momentum quantum number J for the origin at the center of mass and at the helium nucleus. At low energies the cross sections are dominated by the orbiting effects of the long-range attractive polarization forces and the cross section consists of many small contributions from a large number of values of J. Because of interference between the two scattering trajectories, the quantal transition probabilities oscillate, and although at individual values of J the transition probabilities for the two choices of coordinate origin differ considerably, the weighted sums tend to average the differences to zero. Thus the inclusion of translation factors may not be necessary for the calculation of the total cross section at energies in the orbiting region.

In the intermediate energy region between about 3 and 70 eV, $|S_{12}^J|^2$ is a smoothly oscillating function of J, as Fig. 3(b) illustrates. The periods of the oscillations are similar for the two origins, but their amplitudes at small impact parameters are sensitive to the coupling matrix elements and large differences occur in the cross sections for the two origins. At an energy of 13.6 eV the cross section corresponding to the helium nucleus as origin is about thirty times larger than the cross section corresponding to the neon nucleus as origin.

At higher energies above about 70 eV but below some high-energy limit where the inclusion of translation factors is mandatory, the transition probabilities are not sensitive to the coupling matrix elements and, as Fig. 3(c) demonstrates for $E=95.2$ eV, $|S_{12}^J|^2$ is nearly independent of the coordinate origin as are the cross sections.

The behavior of some of these cross sections in the intermediate and higher-energy regions is illustrated by the Demkov[13] model of the process. We assume that transitions between the molecular states take place in a region around a nuclear separation R_C such that the exponentially decaying coupling potential $V_{12}(R_C)$ equals one half of

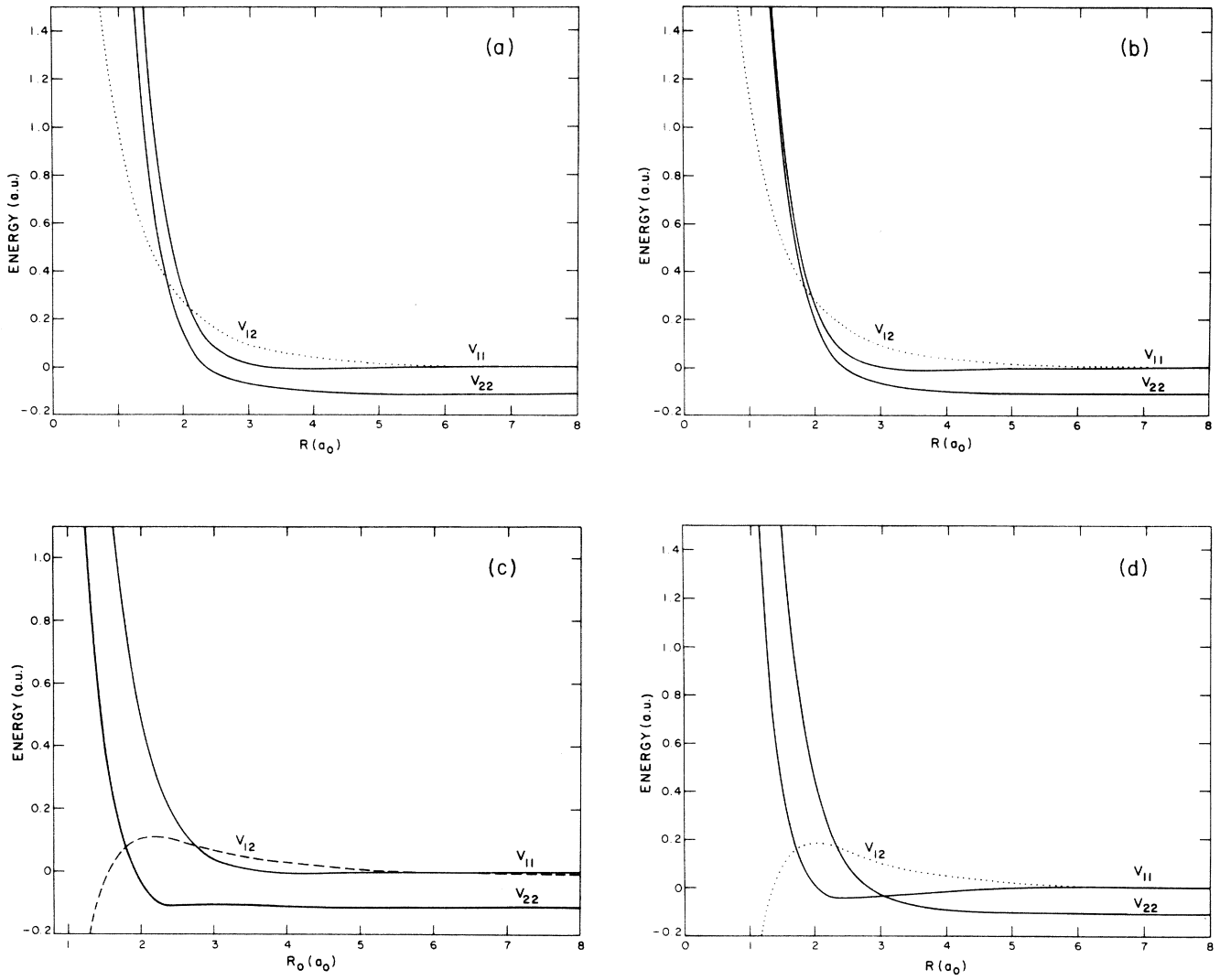

FIG. 2. The elements V_{11}, V_{12}, and V_{22} of the diabatic matrix corresponding to the origin at (a) the neon nucleus, (b) the center of mass, (c) the point on the internuclear axis corresponding to $\eta=(M_1-M_2)/(M_1+M_2)$, and (d) the helium nucleus.

the energy defect $\Delta E(R_C)$ taken to be a constant. At an impact parameter b, the transition probability $P(b)$ is given by[13]

$$P(b)=\operatorname{sech}^2\left[\frac{\pi\Delta E(R_C)}{2\lambda v(b)}\right]\sin^2\left[\int_{-\infty}^{+\infty}V_{12}(t)dt\right], \quad (19)$$

where $\lambda=1.12a_0$ is a parameter representing the exponential decrease at large R of the calculated coupling potential $V_{12}(R)$, v is the relative radial velocity at R_C, and $t=vb$. If V_{12} is large, we may write

$$P(b)=\tfrac{1}{2}\operatorname{sech}^2\left[\frac{\pi\Delta E(R_C)}{2\lambda v(b)}\right]. \quad (20)$$

For the origin at the location corresponding to $\eta=(M_1-M_2)/(M_1+M_2)$, we find that $R_C=3.44a_0$ and $\Delta E(R_C)=2.82$ eV [see Fig. 2(c)], and for the origin at the center of mass $R_C=3.90a_0$ and $\Delta E(R_C)=2.38$ eV.

The Demkov model is appropriate only for impact parameters much less than R_C. In Table II we compare for the two origins the partial cross sections

$$\sigma_p=2\pi\int_0^{R_{\max}}bP(b)db \quad (21)$$

and the corresponding quantal form

$$\sigma_p=\frac{\pi}{2\mu E}\sum_J^{J_{\max}}(2J+1)|S_{12}|^2, \quad (22)$$

where $J_{\max}=\mu R_{\max}v(R_{\max})$, and $R_{\max}$ has the arbitrary value of 0.5. The Demkov model reproduces the quantal cross sections to within a factor of 2 for the entire range of energies between 28 eV and 8 keV, and represents satisfactorily the influence of the choice of origin. Equation (20) shows that in the region around $E=27$ eV, where the argument in parentheses is large and the transition probability is low, small changes in the argument cause large changes in the transition probability. At larger collision energies the argument becomes small and the mean proba-

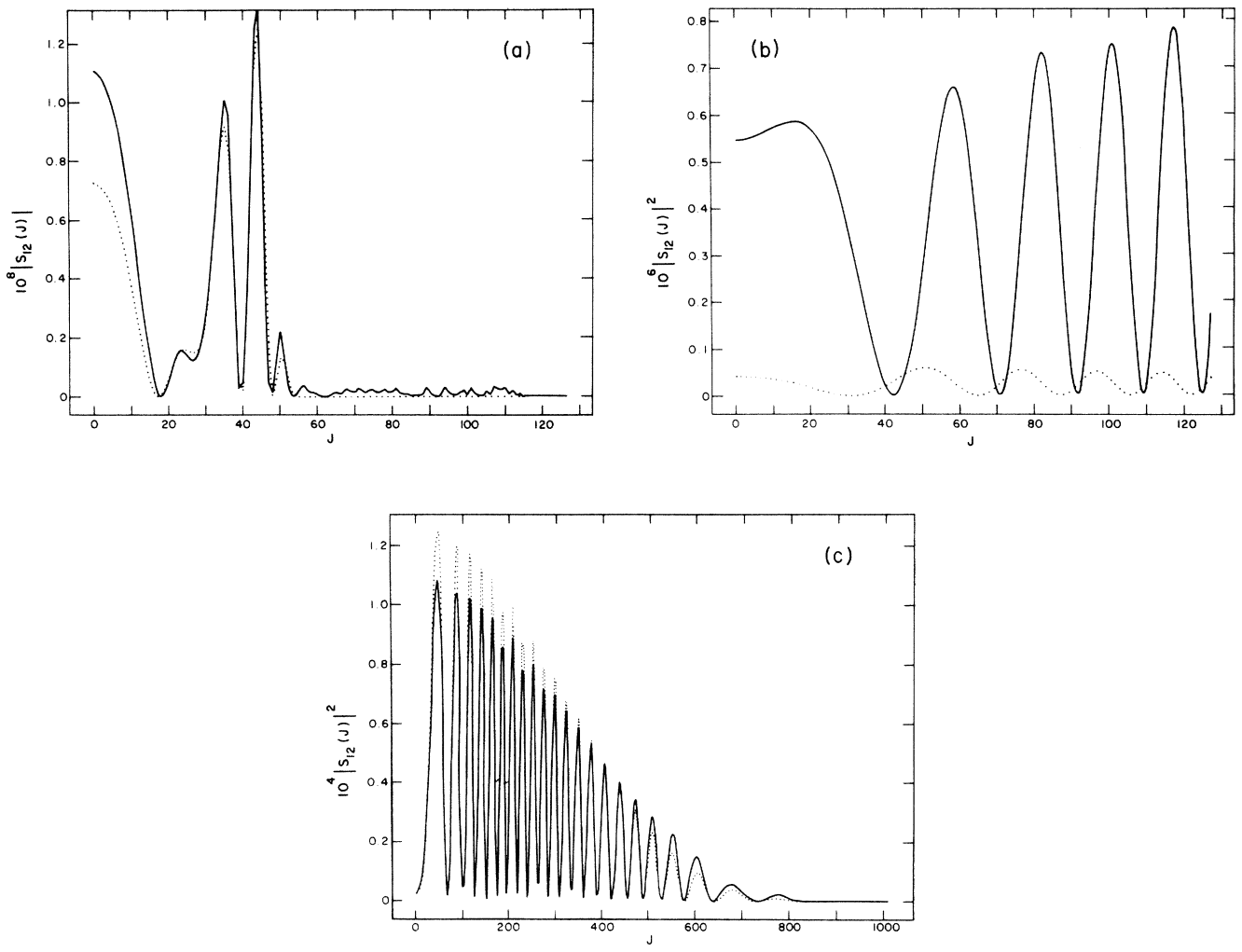

FIG. 3. Transition probabilities $|S_{12}^J|^2$ corresponding to the origin at the center of mass (. . . .) and the helium nucleus (——) at collision energies of (a) 0.272 eV, (b) 13.6 eV, (c) 95.2 eV.

bilities tend to the same value. At much higher energies, the form (19) must be used and the cross sections depend on the behavior of $V_{12}(R)$ at small distances. Our calculations suggest that the energies at which translation factors are crucial lie above 900 eV at which energy we predict a cross section of 1×10^{-16} cm^2 independent of coordinate origin.

The cross sections for radiative charge transfer and radiative association have been calculated for thermal energies.[2] At higher energies, their efficiencies depend upon the ratio of the collision time to the radiative lifetime and we may approximate the cross section sum for the two processes with the formula

$$\sigma_\gamma(E)=1\times10^{-15}v^{-1}\ \text{cm}^2\ , \tag{23}$$

where v is the relative velocity. Thus direct charge transfer is the dominant process at energies above 25 eV.

TABLE II. Partial cross sections σ_p in atomic units (a_0^2).

	$\eta=\frac{M_1-M_2}{M_1+M_2}$		Center of mass	
Energy (eV)	Quantal	Demkov	Quantal	Demkov
27.2	1.5×10^{-7}	1.5×10^{-7}	2.1×10^{-6}	1.5×10^{-6}
109	5.0×10^{-4}	9.4×10^{-4}	1.8×10^{-3}	8.0×10^{-4}
1091	0.11	0.15	0.15	0.14
8160	0.32	0.35	0.34	0.34

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