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Effect of Long-Range Forces in Near-Resonant Charge Transfer: Application to $He^{+}+K$, Rb, and Cs†

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Near-resonant charge transfer in asymmetric collisions is often dominated by long-range forces due to polarization and sometimes to ion-quadrupole interactions. These interactions can lead to regions of strong coupling at large distances. The parameters necessary for estimating the cross sections by a modified Demkov formula (for strong coupling without crossing) can be obtained from a knowledge of simple atomic properties such as ionization potentials and polarizabilities. These formulas are applied to the calculation of the cross sections for the $He^{+}+K$, Rb, and Cs asymmetric charge-transfer reactions and are compared with the experimental measurements of Peterson and Lorents. For these systems several inelastic channels are open and the theory predicts the relative abundances of the various excited states of He ($n=2$).

I. INTRODUCTION

A number of measurements in the last few years have demonstrated that large cross sections are often associated with near-resonant charge-transfer processes.[1–5] Reactions of this type often leave one of the products in an excited state, and this property is now being exploited to produce beams of excited neutrals in specific radiating or metastable states.[6] In one case of charge transfer between a positive and a negative ion, this process has been used to produce laser action.[7]

Among the systems that have been studied in charge transfer between ions and neutrals, particular attention has been devoted to the reactions of H^{+} and of positive ions of the rare gases with various alkali metals.[8–10] Certain molecular ions such as N_2^{+} have also been used.[11] The difference in ionization potentials between the alkali metals and the rare gases or H leads to the common occurence of near resonances for reactions terminating in excited final states. Peterson and Lorents,[5] in a study of total charge transfer between certain rare-gas ions and alkali-metal atoms, have shown that the total cross sections observed (summed over all final states, i.e., without measurement of specific radiating states) were far higher than would be expected for charge transfer into ground-state products, but that they could be explained by assuming that the products were in certain excited states. This conclusion was supported by some estimates based on the Rapp–Francis approximation.[12] They recognized that the theory is not strictly applicable to a case where several competing final states are available, and they suggested that a curve-crossing mechanism might be useful in discussing these processes.

Peterson and Lorents pointed out that the cross sections would be affected not only by the near-resonance condition, but also by the nature of the orbitals involved in the electron transfer, and they stated: "In the reactions involving He^{+} ions studied here, near-resonant reactions can yield either excited He atoms or excited alkali ions. However, excitation of the final ion involves at least one closed-shell electron of the ion and perhaps the valence electron as well. At these comparatively low energies such events are probably less frequent than the electron transfer producing excited He atoms, which need only be an outer electron process."

Salop, Lorents, and Peterson[11] have now measured the optical excitation produced in some of these same systems and their results confirm the effects predicted in the earlier work of Ref. 5. These effects appear to represent general principles of considerable importance for a very large class of charge-transfer reactions with large cross sections.

In charge transfer at large internuclear separations, essentially we are dealing with electron transfer between two perturbed, but almost free, atoms or ions. In contrast, as Peterson and Lorents pointed out, excitation out of an inner shell (when, for instance, an excited alkali ion is produced) requires a close encounter and involves interactions in the region of molecular coupling where the assumptions of atomic coupling are no longer valid. To treat these close encounters requires detailed molecular-state calculations, and they will not be discussed here. Moreover charge-transfer processes that occur at small internuclear separations will not produce the magnitude of the cross sections we will be discussing here, $Q \gtrsim 100$ Å^2. Thus, although these processes do occur, charge transfer at close encounters will contribute only a small share to the over-all charge-transfer total cross section.

It is obviously of great interest to attempt to translate the intuitive and qualitative arguments of

Ref. 5 into a more quantitative (even if approximate) form in order to provide a framework for the evaluation of experiments and for the prediction of similar effects in other systems.

The principal aim of this paper is to show that a quantitative treatment of charge-transfer reactions at large distances can, in fact, be derived in very simple form if we make use of the fact that the principal long-range forces are due to polarization of the neutral by the ion supplemented, when the neutral is not an atom in an *S* state, by the interaction with the quadrupole moment of the neutral. These long-range forces are different in the initial and final states and often give rise to regions of strong interaction at large distances, which provide a route for easy transfer of charge.

Three specific systems are studied: $He^+ + K$, Rb, and Cs. The charge-transfer cross sections are calculated using a modified Demkov theory[13,14] for strong interactions at large distances, and are compared with experimental results.[5,9,10] The parameters necessary for the calculations are obtained from a knowledge of the properties of the separated collision partners, such as ionization potentials, excitation potentials, polarizabilities, and quadrupole moments. Reasonable agreement between theory and experiment is obtained for $He^+ + K$ and $He^+ + Rb$, but there are substantial differences in the $He^+ + Cs$ case. Possible reasons for the discrepancies are discussed in later sections.

II. THEORY

The theoretical treatment of the $He^+ + K$, Rb, and Cs systems is complicated by the fact that charge transfer results in the production of several different excited states. Furthermore, the interactions between reactant and product states cannot be treated theoretically by assuming constant potentials and using the infinite separation energies as the separation between channels. In the systems investigated here, we have considered the effects of the long-range polarization and quadrupole forces to estimate the regions of strong interaction between reactant and product channels. Inclusion of these long-range forces and the use of a more accurate method to estimate the cross sections[14] cause our predictions of the excited-state products and the magnitude of the total cross sections to differ appreciably with previous theoretical estimates.[15]

A simplifying characteristic of the He^+ + alkali systems, however, is that the reactant states are divided between molecular states of $^1\Sigma$ and $^3\Sigma$ symmetry. This separation allows us to generally use two-state procedures, since the number of product states of a given symmetry is then considerably reduced.

The specific reactions that we will be studying in this paper are

$$He^+ + A \rightarrow He^* + A^+ + \Delta E \ , \tag{1}$$

where *A* can be K, Rb, or Cs and where He* represents an excited level of the He atom. At large distances, where the major share of charge transfer occurs, the interaction potentials are written

$$V_i(R) = V_i(\infty) - \frac{\alpha_i e^2}{2R^4} - \frac{\beta_i e^2}{R^3} \ , \tag{2}$$

where $V_i(\infty)$ is the sum of the excitation and ionization energies of the separated collision partners measured from a common origin. The dipole polarizability is given by α_i, and the β_i is the ion-quadrupole moment of the neutral partner in either state.

A modified Demkov approach[13,14] can be applied to reaction (1) to calculate the cross sections. In this model the reactant and product potential curves are assumed to be parallel with one another, and the coupling-matrix element is assumed to have an exponential *R* dependence. Charge transfer at low to moderate energies is then found to be localized at the internuclear separation R_c where the difference in potential curves is equal to twice the coupling-matrix element

$$H_{12}(R_c) = \tfrac{1}{2}\left| V_1(R_c) - V_2(R_c)\right| = \tfrac{1}{2}\Delta V(R_c) \ . \tag{3}$$

Before this model can be applied, it is necessary that we have a reasonable estimate of the coupling-matrix element $H_{12}(R)$. The coupling-matrix element calculation was performed using the formula[16]

$$H_{12}(R) = I_1^{1/2} I_2^{1/2} R^* e^{-0.86R^*} \ , \tag{4}$$

where

$$R^* = \tfrac{1}{2}(\alpha + \gamma)R \ .$$

In Eq. (4), $\frac{1}{2}\alpha^2$ equals the effective ionization potential I_1 of the atom of Eq. (1) in the reactant state, and $\frac{1}{2}\gamma^2$ equals the effective ionization potential I_2 of the atom in the product state, with all quantities being in a.u.

The total charge-transfer cross sections are then calculated as a function of velocity for the various reactant-product-state combinations using Ref. 14, which gives the cross sections in terms of a reduced velocity

$$\delta^{-1} = \frac{2\hbar\lambda v_0}{\pi\Delta V(R_c)} \tag{5}$$

and in terms of a reduced cross section

$$Q^* = Q/\tfrac{1}{2}\pi R_c^2 \ . \tag{6}$$

In Eq. (5), v_0 is the incident velocity and λ is the coupling-matrix-element exponential-decay factor, $\lambda = 0.86(\alpha + \gamma)/2$.[17]

III. APPLICATIONS

A. $He^+ + K$ System

The first system to be studied is the charge-transfer reaction

$$He^+ + K \rightarrow He^* + K^+ + \Delta E \ , \tag{7}$$

where He^* denotes excited $n = 2$ levels of He. In the energy range studied here, $E \lesssim 1500$ eV, it is expected that the other possible channels for this reaction,

$$He^+ + K \rightarrow He + K^{+*} + \Delta E \ , \tag{8}$$

will contribute less than 5% to the over-all total charge-transfer cross section. For $He^+ + Rb$ at a collision energy of 1470 eV, Salop, Lorents, and Peterson[11] estimate that excitation to the excited levels of Rb^+ contributes less than 4% to the cross section. The arguments first made by Peterson and Lorents[5] that the excitation of the alkali ion is much less probable than excitation of the helium atom should apply to all the systems studied here for energies less than about 1 keV. At higher energies, however, these arguments may not hold. As the collision energy is increased much above 1 keV, the conditions necessary for leaving the alkali ion in reaction (8) in an excited state become much more favorable. Excitation of the alkali ion requires charge transfer of the outer s electron and then excitation of a p electron of the alkali ion. This latter process becomes probable at the higher energies for small impact-parameter collisions, since it requires excitation of an inner-shell electron.

In reaction (7), the first four excited levels of helium are predominantly populated. Table I gives the parameters necessary for calculating the cross sections. It must be remembered, moreover, that the triplet states have a statistical weight of $\frac{3}{4}$, while the singlet states are weighted by $\frac{1}{4}$. For both of the $1s2s$ states the dipole polarizabilities were obtained from Victor, Dalgarno, and Taylor,[18] while the dipole polarizability of the alkali atom was obtained from the work of Dalgarno and Kingston.[19] The dipole polarizabilities for the $1s2p$ states were estimated by scaling the polarizability of the $2s$ state of the same symmetry to the effective ionization potentials of the states involved. The quadrupole moment for $He(2\,^{1,3}P)$ was estimated by scaling from the reported value[20] for $Si^+(^2P)$, $2.85a_0^2$, by using the ionization potential of $Si^+ \rightarrow Si^{++}$, 16.3 eV, and assuming

$$\beta_{He^*} \approx (\beta_{Si^+})(I_{Si^+}/I_{He^*}) \ . \tag{9}$$

The quadrupole moments estimated by Eq. (9) agree within 10% to the hydrogenic-model results of Krogdahl.[21] All ionization potentials were obtained from the tables of Moore.[22]

TABLE I. $He^+ + K$ cross-section parameters.

State of He	$He(2\,^3S)$	$He(2\,^1S)$	$He(2\,^3P)$	$He(2\,^1P)$
$\Delta V(\infty)$ (eV)	$+0.428$	-0.368	-0.717	-0.971
$\alpha_d(He^*)$ (a_0^3)	316	802	416	945
$\alpha_d(K)$ (a_0^3)	281	281	281	281
$\beta(He^*)$ (a_0^2)	...	...	13.5	13.5
R_c (a_0)	9.4	13.1	10.9	11.6
$H_{12}(R_c)$ (a.u.)	0.0090	0.0047	0.0057	0.0045
λ (a_0^{-1})	0.497	0.475	0.465	0.457
δ^{-1}/v (sec/cm)	8.07(−8)	1.49(−7)	1.20(−7)	1.48(−7)

The over-all comparison between the theoretical cross sections and the measured total charge-transfer cross sections[5] is shown in Fig. 1. The theoretical calculations are in reasonable agreement with the experimental results except at the very low energies, where the theory predicts a more rapid decrease of the cross sections.

B. $He^+ + Rb$ System

The calculations for the charge-transfer reaction

$$He^+ + Rb \rightarrow He^* + Rb^+ + \Delta E \tag{10}$$

are displayed in Fig. 2. The parameters for calculating the cross sections are listed in Table II.

As in the $He^+ + K$ reaction, $He(2\,^3P)$ is the main collision product at energies above 200 eV. A good share of the reason for this is that the triplet states have a $\frac{3}{4}$ statistical weight factor, while the singlets are weighted by only $\frac{1}{4}$.

The over-all total cross section may be compared with experiment.[5] There is good agreement up to 500 eV. Above this energy the theoretical cross sections underestimate the experimental results. Since it was shown that excitation to Rb^{+*} levels leads to less than 4% of the total cross section at 1470 eV, some other source of explanation for the discrepancy must be found.

One mechanism that was not calculated and would be analyzed as a charge-transfer product in the experiment is the ionization reaction

$$He^+ + Rb \rightarrow He^+ + Rb^+ + e + \Delta E \ . \tag{11}$$

At the higher energies, it is probable that reaction (11) could contribute to the experimental cross sections. Also, since we have only calculated the cross sections for the $n = 2$ levels of excited helium, it is probable that the cross sections for higher excited states, $n > 2$, could be sizable.

However, the most probable explanation for the disagreement between theory and experiment lies in the neglect by theory of the rotational coupling of the Σ molecular states of the reactants to the Π molecular states of the close-lying $He(1s2p)$ states. At energies above 1000 eV, it would be surprising if there was not appreciable rotational coupling to

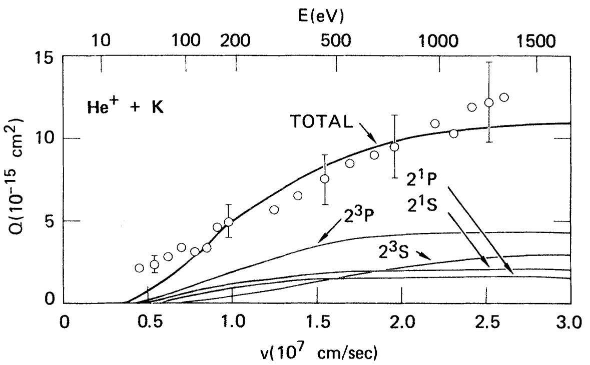

FIG. 1. He$^+$+ K charge-transfer total cross sections. The solid lines are the theoretical calculations with the contribution from the various excited levels of helium designated by their term symbols. The experimental points with their error bars are from Ref. 5.

the Rb$^+$+He($2\,^3P$) state, which has a ΔE of only -0.556 eV.

C. He$^+$ + Cs System

Calculation of the He$^+$+Cs charge-transfer total cross sections is an interesting problem, because there exist not only the low-energy data of Peterson and Lorents,[5] but also measurements at higher energies[9,10] and a state-population measurement[23] at very low energies ($E \approx 10$ eV). Table III presents the parameters necessary to calculate the cross sections shown in Fig. 3.

In Fig. 3 we see very little contribution by the He($2\,^3S$) state, because the Demkov-type interaction is at a relatively small internuclear separation. Within the theoretical framework presented here, there is a negligible contribution from the He($2\,^1S$) state. In Table III we see the reason for this. As the internuclear separation is decreased from large distances, the difference in potential energy between the reactant and product channels actually increases due to the large differences in the dipole polarizabilities. At separations where charge transfer is most probable ($R \sim 5$ to $15a_0$) the potential energy difference is so large that it precludes any reaction. Possibly at short ranges, where the repulsive forces come into play, there can be charge transfer, but this can only contribute a small fraction to the magnitude of the cross sections we are discussing here. This point is interesting in that from a casual look at this reaction one would predict the He($2\,^1S$) state to be highly populated due to its small $\Delta V(\infty)$ value.

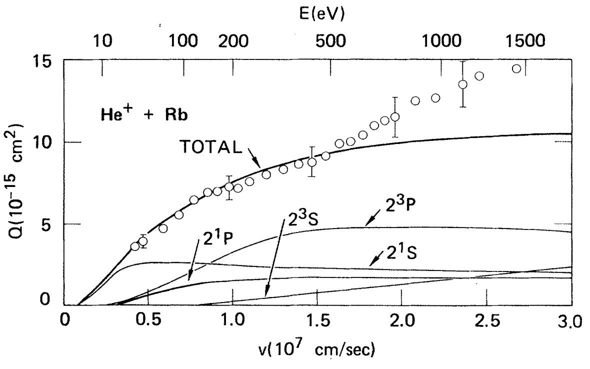

FIG. 2. He$^+$+Rb charge-transfer total cross sections. The solid lines are the theoretical calculations with the contribution from the various excited levels of helium designated by their term symbols. The experimental points with their error bars are from Ref. 5.

TABLE II. He$^+$+Rb cross-section parameters.

State of He	He($2\,^3S$)	He($2\,^1S$)	He($2\,^3P$)	He($2\,^1P$)
$\Delta V(\infty)$ (eV)	$+0.591$	-0.205	-0.556	-0.807
α_d(He*) (a_0^3)	316	802	416	945
α_d(Rb) (a_0^3)	296	296	296	296
β(He*) (a_0^2)	···	···	13.5	13.5
R_c (a_0)	8.7	14.9	11.7	12.2
$H_{12}(R_c)$ (a.u.)	0.012	0.0012	0.0043	0.0038
λ (a_0^{-1})	0.493	0.471	0.460	0.452
δ^{-1}/v (sec/cm)	6.12(−8)	5.78(−7)	1.55(−7)	1.74(−7)

At collision energies of about 10 eV, Dehmelt and Major[23] concluded that their trapped-ion measurements supported the premise that only He($2\,^1S$) metastable atoms were produced in the charge transfer of He$^+$ on Cs. In fact, though, their measurements can only support the conclusion that singlet states of helium are produced in the He$^+$+Cs charge-transfer reaction. At low energies our theoretical calculations predict He($2\,^3P$) and He($2\,^1P$) as the sole products. It is most probable that the He($2\,^3P$) and He($2\,^1P$) states are further populated by $\Sigma - \Pi$ rotational coupling with the reactant channel. As in the Li$^+$+Li[24] and Li$^+$+Na[25] charge-transfer systems, curve crossing between Σ and Π states can give quite large cross sections at low collision energies.[26] This additional coupling would increase the theoretical cross sections for better agreement with experiment. If the

TABLE III. He$^+$+Cs cross-section parameters.

State of He	He($2\,^3S$)	He($2\,^1S$)	He($2\,^3P$)	He($2\,^1P$)
$\Delta V(\infty)$ (eV)	$+0.874$	$+0.078$	-0.271	-0.525
α_d(He*) (a_0^3)	316	802	416	945
α_d(Cs) (a_0^3)	363	363	363	363
β(He*) (a_0^2)	···	···	13.5	13.5
R_c (a_0)	8.4	···	13.8	13.5
$H_{12}(R_c)$ (a.u.)	0.014	···	0.0021	0.0025
λ (a_0^{-1})	0.485	···	0.452	0.444
δ^{-1}/v (sec/cm)	5.18(−8)	···	3.20(−7)	2.62(−7)

$He(2^1P)$ is predominantly populated, there would then be agreement with the conclusions of Dehmelt and Major.[23]

The poor agreement with experiment above 200 eV can most probably be explained in the same manner as in the $He^+ + Rb$ system, where we attributed the cause to the neglect of the long-range rotational coupling. For the $He^+ + Cs$ system we would expect rotational coupling to be more important at lower energies than in the $He^+ + Rb$ system, because the $He(1s2p)$ levels are now becoming more resonant with the reactant state (Tables II and III). Moreover, the magnitude of the disagreement indicates that some process occurring at large separations is being neglected by our treatment. Hence, at the higher collision energies we would predict that the populations of $He(2^3P)$ and $He(2^1P)$ are underestimated by these calculations.

Work has begun with J. C. Browne at the University of Texas at Austin to calculate the cross sections for rotational coupling using coupling-matrix elements obtained from *ab initio* potential calculations. We will be studying this specific problem further in the near future.

We can compare our calculations with experiments performed at higher energies[9,10]; the results are shown in Fig. 4. The over-all agreement between theory and experiment is fair. It does appear, however, that the low- and high-energy experimental measurements are not in too good agreement with one another.

The theoretical estimations of the $He^+ + Cs$ cross sections were checked by performing coupled two-state calculations of the transition probabilities and then integrating these probabilities over the impact parameter to obtain the cross sections. The method used was the forced-common-turning-point procedure of Bates and Crothers.[27] The singularity at the turning point was removed by utilizing the change of variables suggested by Bates and Sprevak.[28] The agreement between the cross sections calculated by the approximate methods and those calculated by the numerical procedure was better than 0.5×10^{-15} cm^2. This lends considerable validity to using the modified Demkov method to calculate these charge-transfer total cross sections.

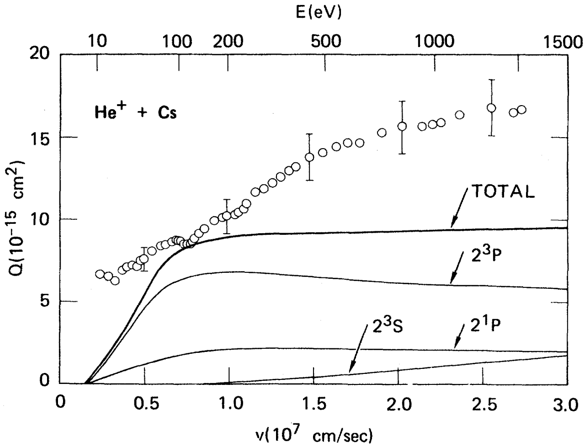

FIG. 3. $He^+ + Cs$ charge-transfer total cross sections. The solid lines are the theoretical calculations with the contribution from the various excited levels of helium designated by their term symbols. The experimental points with their error bars are from Ref. 5.

IV. CONCLUSIONS

Near-resonant charge-exchange total cross sections were calculated for the $He^+ + K$, Rb, and Cs systems and compared with experimental results. A modified Demkov[13,14] method was used to calculate the cross sections. For the $He^+ + Cs$ system, two-state coupled-channel calculations were used to compare with the approximate theoretical methods, and good agreement was found.

Fair agreement between theory and the experiments of Ref. 5 was found in the $He^+ + K$ system. For $He^+ + Rb$ the theoretical results underestimated the cross sections at energies above 500 eV, and for $He^+ + Cs$ at energies above 200 eV. Since it was shown experimentally for $He^+ + Rb$ that the excited-alkali-ion ground-state-helium products contribute very little to the over-all total cross section,[11] we believe the discrepancy lies in the neglect of the rotational coupling to the $He(2\,^3P)$ and $He(2\,^1P)$ states. For the series K → Rb → Cs, the helium $2p$-state products are becoming more resonant with the reactant channel. We would therefore expect that the neglect of rotational coupling would cause the theory to underestimate the cross sections at lower and lower energies as the alkali atom becomes heavier. This is the trend observed in Figs. 1–3.

One of the more surprising results of the calculations is that $He(2^1S)$ is not populated to an appreciable extent in collisions of He^+ on Cs. Any simple theory based only on the energy separations at infinite R would say that the contribution to the total cross section by this state would be appreciable, since it has the smallest ΔV $(R = \infty)$ of the excited He states (Table III). However, when the polarization potentials are taken into account, we find very little contribution by this state, because the reactant and product channels actually separate slowly as R is decreased, precluding the possibility of charge transfer.

Another point to make is that the state populations of the products become more statistical at the higher energies, $E \gtrsim 1$ keV. That is, the triplet-state products are three times more abundant than the singlet-state products. This is caused by a more or less equal mixing of the states at the higher energies, leading to the cross sections for the various

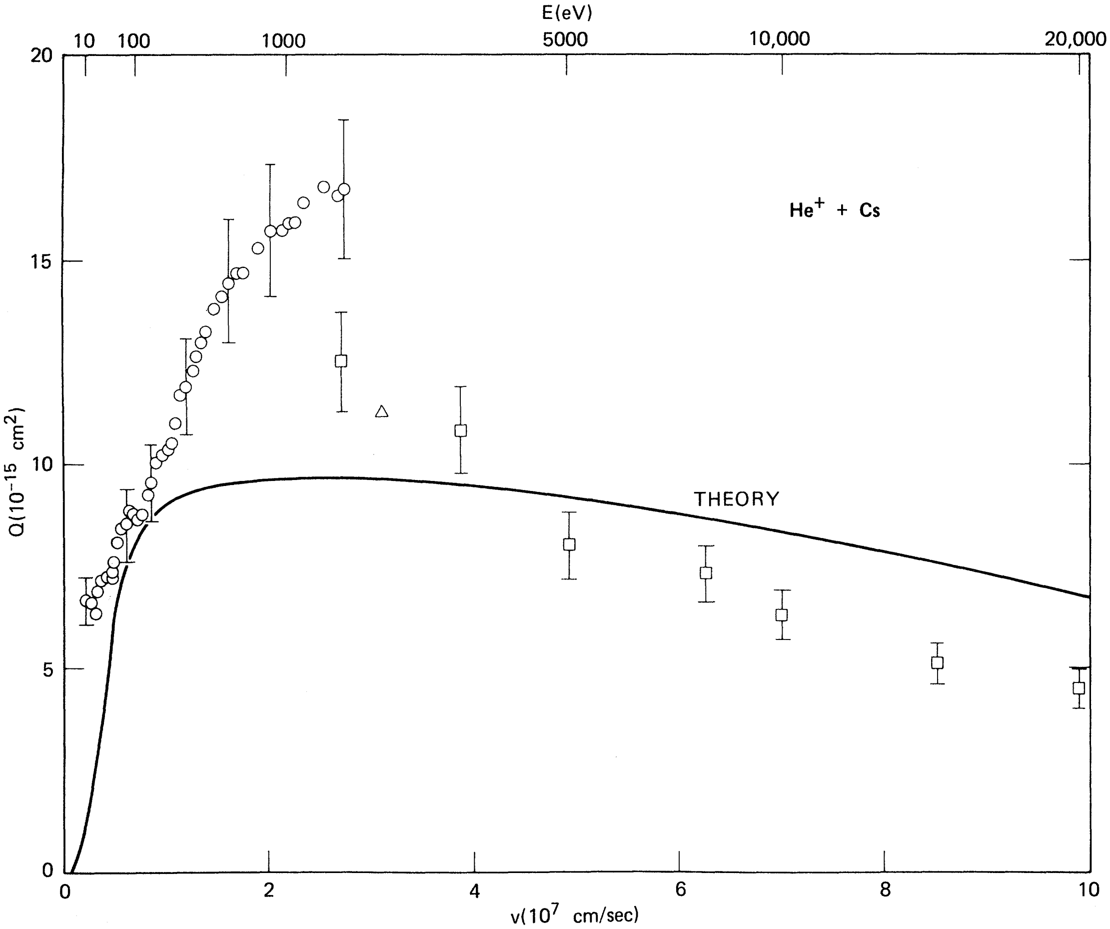

FIG. 4. He$^+$ + Cs charge-transfer total cross sections over a larger velocity range. The theoretical curve is compared with the experimental points of Refs. 5 (open circles), 9 (open triangle), and 10 (open squares).

products being heavily determined by their statistical weights. At the low energies, however, only rarely are the triplet-to-singlet ratios found to be equal to 3. Here, one must consider the actual dynamics of the collision to determine the triplet-to-singlet ratio.

Because of the methods used in our calculations, we did not consider phase effects that can lead to oscillations on the total cross sections. There does appear, however, to be a hint of oscillatory structure of the He$^+$+Cs experimental cross sections (Fig. 3). The oscillation frequency is roughly proportional to the reciprocal velocity, as one would expect, if there exists a long-range Stark mixing of the potential curves[29] or an extremum in the difference potentials within the coupling region.[30]

In Figs. 1–3 we have also shown the contributions of the various excited product states to the over-all total cross section. In the near future, experimental measurements will be performed that will test these predictions.[31]

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Electron Emission in H_2^+-H_2 Collisions from 0.6 to 1.5 MeV[*]

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Cross sections, differential in emission energy and angle, have been measured for the ejection of electrons in collisions of H_2^+ ions with molecular hydrogen. Incident-ion energies studied were 0.6, 1.0, and 1.5 MeV and electron emission was measured over the laboratory angular range of 20°–125°. Electron-emission cross sections are compared with measurements for incident protons having the same velocity as the H_2^+ ions. Electron distributions attributable to dissociative ionization of the H_2^+ ion are integrated to obtain the total cross section for dissociative ionization. A comparison is made between measured differential cross sections for scattering the bound electron of the incident ion and cross sections for scattering of incident free electrons.

I. INTRODUCTION

Experimental electron-emission cross sections, differential in ejected electron energy and angle, provide sensitive tests of the reliability and limitations of theoretical treatments of the ionization process. Cross sections for electron emission by protons have been measured for proton energies from 0.05 to 2.0 MeV for a wide range of gas targets.[1–7] These measured cross sections, when compared with theoretical predictions, have provided information concerning the relative importance of various interactions which enter into a complete description of ionization by fast charged particles.[8–12] Very few measurements of doubly differential electron-emission cross sections have been made, however, for incident particles which possess an electronic or molecular structure in themselves. Cacak[13] has measured electron distributions of Ne-Ne and Ar-Ar collisions for ion energies of 50–300 keV and autoionization Auger electron emission has been studied for Ar, Ne, He, and H_2^+ impact.[14–16] To our knowledge, the autoionization studies with H_2^+ impact are the only published measurements of electron distributions resulting from an incident molecular ion.[14]

Electron distributions from molecular-ion impact can be used to obtain information regarding collisional dissociation of the incident ion as well as ionization of the target. When fast molecular-hydrogen ions (H_2^+) collide with a target molecule any of several modes of dissociation of the incident ion are possible:

$$H_2^+ \rightarrow H + H^+ , \tag{1}$$

$$H_2^+ \rightarrow H^+ + H^+ + e , \tag{2}$$

$$H_2^+ + e \rightarrow H + H , \tag{3}$$

and each reaction may be accompanied by excitation and/or ionization of the target atom or molecule.

McClure and Peek have recently critically reviewed the extensive published work on dissociative collisions of heavy particles, especially H_2^+