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Molecular-state cross-section calculations for $H+Cs\rightleftharpoons H^-+Cs^+$

R. E. Olson, M. Kimura, and H. Sato*
Physics Department, University of Missouri-Rolla, Rolla, Missouri 65401

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Pseudopotential molecular-structure calculations have been used to obtain the seven lowest $^1\Sigma$ and $^1\Pi$ states of CsH. These states and their associated radial and rotational coupling terms have been used to calculate the cross sections for H^-+Cs^+ ion-pair production in $H+Cs(6s)$ and $H+Cs^*(6p)$ collisions at energies from 0.1 to 10 keV. The ion-ion mutual neutralization cross section, $H^-+Cs^+\rightarrow H+Cs$, is also presented. The cross-section calculations were done with the perturbed-stationary-state method, modified to include two-electron translation factors. The ion-pair production cross section for ground-state reactants is in good agreement with experiment; collisions of H with excited $Cs^*(6p)$ show an order-of-magnitude enhancement of the ion-pair production cross section at 100 eV. The ion-ion mutual neutralization cross section is found to be large, attaining a value of 1.3×10^{-14} cm^2 at 0.1 keV.

INTRODUCTION

The cesium hydride (CsH) system has attracted considerable interest in recent years. Part of the reason for this interest is due to the fact that the ground molecular state of CsH is deeply bound, $D_e\approx1.87$ eV, due to the influence of strong ion-pair formation (H^-+Cs^+) at the equilibrium separation. Correspondingly, collisions of H with Cs at moderate energies, $E\approx1$ keV, lead to the formation of H^- with a relatively large cross section of the order of 10^{-16} cm^2.[1-5] This collisional property can be exploited to produce intense beams of H^- and D^- which can be used to heat and fuel fusion reactors.[4]

Theoretical interest in CsH includes the analysis of spectroscopic data to accurately determine the $X\,^1\Sigma$ and $A\,^1\Sigma$ molecular potentials of CsH (Refs. 6–8) and the use of asymptotic expansion to calculate the potential differences at the avoided curve crossings between the H^-+Cs^+ and $H+Cs^*$ states.[9-11] Molecular-structure calculations on CsH generally use the pseudopotential method.[12,13] The reason for this choice is that nonrelativistic *ab initio* calculations using the Hartree-Fock method underestimate the ionization potential of the Cs atom by ~0.6 eV.[14] Large configuration-interaction (CI) calculations on Cs decrease this discrepancy by only a factor of 2. For scattering calculations on CsH, it is essential that the molecular states dissociate to their correct limits relative to one another. Otherwise, the locations of the avoided curve crossings are incorrect and the scattering results are subject to considerable suspicion.

In this work we have performed molecular-structure calculations that utilize a pseudopotential to represent the 54-electron ion core of Cs. Intermolecular potentials and wave functions were calculated for the low-lying $^1\Sigma$ and $^1\Pi$ states of CsH. The wave functions were used to calculate the radial and rotational coupling matrix elements for use in a perturbed-stationary-state calculation. Electron-translation-factor corrections were incorporated in the coupling terms. Cross sections were calculated at energies from 100 eV/amu to 10 keV/amu for ion-pair formation from the ground state,

$$H+Cs(6s)\rightarrow H^-+Cs^+\ , \tag{1}$$

and from the first excited state of Cs:

$$H+Cs^*(6p)\rightarrow H^-+Cs^+\ . \tag{2}$$

The cross section for the reverse reaction, ion-ion mutual neutralization was also evaluated:

$$H^-+Cs^+\rightarrow H+Cs\ . \tag{3}$$

It should be noted that the cross section for reaction (3) cannot be obtained by detail balance from either reaction (1) or (2) because the products of ion-ion mutual neutralization are not a single electronic level, but a mixture of the $Cs(6s)$, $Cs(6p)$, and $Cs(5d)$ states.

Other attempts have been made to calculate the cross sections for reaction (1). The first attempt used crude potentials and wave functions and obtained poor results.[15] A subsequent calculation[16] that employed Rydberg-Klein-Rees (RKR) potential curves and the matrix elements from Ref. 15 realized similar results. A latter two-state quantum-mechanical calculation[17] that used RKR potentials in cross-section evaluations at low energies is in good agreement with recent experimental data.[3]

In this work we present coupled-channel calculations for the cross sections of reactions (1)—(3) using recently developed theoretical techniques. The calculations are benchmarked against experiment for reaction (1) and predictions are made as to the cross sections for reactions (2) and (3).

MOLECULAR STRUCTURE

The details of the theoretical treatment have been presented,[18] so we will only outline the basic techniques and the specific information used for the CsH calculations. For the collision energy range of interest in this work, we have employed the perturbed-stationary-state method with electron translation factors[18] appropriate for a pseudo-two-electron system. The molecular energies and wave functions were calculated using a linear combination of Slater determinants. Slater-type orbitals were employed.

For the CsH molecular calculations, the Cs^+-ion core was represented by an l-dependent pseudopotential of the form

$$V(\vec{r})=\sum_{l,m} V_l(r)\,|\,Y_{lm}\rangle\langle Y_{lm}\,| \tag{4a}$$

with

$$V_l(r)=A_l\exp(-\xi_l r^2)-\frac{\alpha_d}{2(r^2+d^2)^2}-\frac{\alpha_q}{2(r^2+d^2)^3}-\frac{1}{r}\,. \tag{4b}$$

The dipole and quadrupole polarization terms allow some polarization of the ion core. The parameters A_l and ξ_l of the Gaussian term are determined by a fit to spectroscopic data. The parameters have been determined by Bardsley[19] and are reproduced in Table I as a convenience to the reader.

The orbital exponents of the Slater-type-orbital basis set are given in Table II. The hydrogen basis set and the $5s$, $6s$, and $6p$ terms of cesium are from the work of Stevens *et al.*[12] We have added two additional d orbitals and a $7s$ orbital whose exponents were determined by optimizing for the lowest energies of the $Cs(5d)$ and $Cs(7s)$ states, respectively. The calculated ionization energies of the cesium $6s$, $6p$, $5d$, and $7s$ atomic levels reproduce spectroscopic data to within 0.01 eV. (Note: we did not include spin-orbit effects in these calculations.) The electron affinity of hydrogen is underestimated by 0.089 eV from the recommended value of 0.754 eV. Additional $3d$ orbitals and electron correlation would be necessary to reduce this error. We deemed such an error is acceptable for the scattering calculation by inspecting the changes in the curve-crossing radii if the ion state were shifted downward by the 0.089 eV.

A complete two-electron configuration interaction calculation (all possible single and double electron excitations) was performed to obtain the molecular structure for the low-lying $^1\Sigma$ and $^1\Pi$ states. The interaction energies are presented graphically in Fig. 1. Note, the triplet molecular states were not needed for the scattering calculations. We have, however, included the appropriate statistical weight factor on the initial channels for the ion-pair formation cross sections to encompass the fact that only 25% of the flux starts on the singlet states.

TABLE I. Pseudopotential parameters in atomic units for Cs^+.

A_0	14.767 32
A_1	2.960 707
A_2	−0.399 982
A_3	−1.943 567
ξ_0	0.541 614
ξ_1	0.232 594
ξ_2	0.193 255
ξ_3	0.367 542
α_d	15.0
α_q	230.0
d	2.0

TABLE II. Slater-type-orbital basis set.

H 1*s*	1.218	Cs 5*s*	1.620
	0.463		
		6*s*	1.569
2*s*	1.058		0.903
			0.494
2*p*	1.058		
	0.309	6*p*	1.200
			0.743
		7*s*	0.302
		3*d*	1.149
			0.467

Of importance for scattering calculations are the positions and potential-energy differences at the avoided curve crossings between the ion-pair and covalent states. In Table III we summarize the results of our calculations and compare them to others. For the avoided crossing between the $1\,^1\Sigma$ and $2\,^1\Sigma$ states, our calculations are in good agreement with the analysis of spectroscopic data by Hsieh *et al.*[6] The position of the avoided crossing between the $2\,^1\Sigma$ and $3\,^1\Sigma$ states calculated by us appears to be too large when compared to the analysis of spectroscopic data by Yang *et al.*[8] This avoided crossing is quite broad so that slight differences are accentuated. The energy splitting appears reasonable, however. The parameters of the long-range avoided crossing between the $3\,^1\Sigma$ and

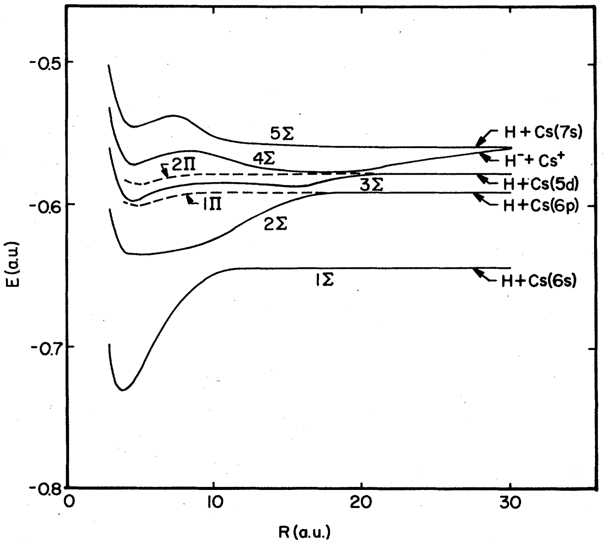

FIG. 1. Calculated singlet molecular-state interaction energies for the CsH system. These seven states were used in the cross-section evaluations.

TABLE III. Positions and energy differences at the avoided curve-crossings between ionic and covalent channels.

State	Reference	Method	$R_x(A_0)$	$\Delta V(R_x)$ (eV)
H + Cs(6s)	This work	CI	9.8	0.656
	Hsieh *et al.* (Ref. 6)	Spectroscopic	9.73	0.632±0.037
	Laskowski and Stallcop (Ref. 13)	CI	~10.0	~0.80
	Olson *et al.* (Ref. 15)	CI	9.9	0.82
	Adelman and Herschbach (Ref. 10)	Asymptotic	9.74	0.75
	Janev and Radulovic (Ref. 11)	Asymptotic	9.74	0.602
H + Cs(6p)	This work	CI	16.7	0.216
	Yang *et al.* (Ref. 8)	Spectroscopic	15.94	
	Olson *et al.* (Ref. 15)	CI	16.3	0.28
	Adelman and Herschbach (Ref. 10)	Asymptotic	15.81	0.25
	Janev and Radulovic (Ref. 11)	Asymptotic	16.2	0.226
H + Cs(5d)	This work	CI	19.9	0.0786
	Adelman and Herschbach (Ref. 10)	Asymptotic	20.4	0.0610

$4\,^1\Sigma$ states compare well to the asymptotic expansion method of Adelman and Herschbach.[10]

CROSS SECTIONS

The scattering calculations on the CsH system included the seven $^1\Sigma$ and $^1\Pi$ molecular states shown in Fig. 1. All possible combinations of the radial and rotational coupling terms were included in the cross-section evaluations. A representative set of the coupling terms is displayed in Fig. 2. The radial matrix elements are peaked at the avoided curve crossings.

The close-coupled equations were solved numerically. The electron-translation-factor corrections were retained to first order in velocity. Classical trajectories were used for the heavy-particle motion. A straight-line trajectory was used for H + Cs(6s) and H + Cs*(6p) initial channels, reactions (1) and (2), while an attractive Coulomb trajectory was used for the H^- and Cs^+ initial channel, reaction (3).

The cross-section calculations for ion-pair formation in H + Cs(6s) collisions, reaction (1), are shown in Fig. 3 along with available experimental data. There is good agreement that the maximum in the cross section occurs at ~500 eV/amu with a value of $\sim 9\times10^{-16}$ cm^2. At higher energies there is also general agreement between theory and experiment. At low energies our theoretical calculations are in good agreement with Miethe *et al.*[3] who made a systematic check of the angular scattering of H^- to ascertain that all the negative ions were detected. We are in reasonable agreement with the data of Meyer,[1] except at the lowest energy. Meyer used an attenuation

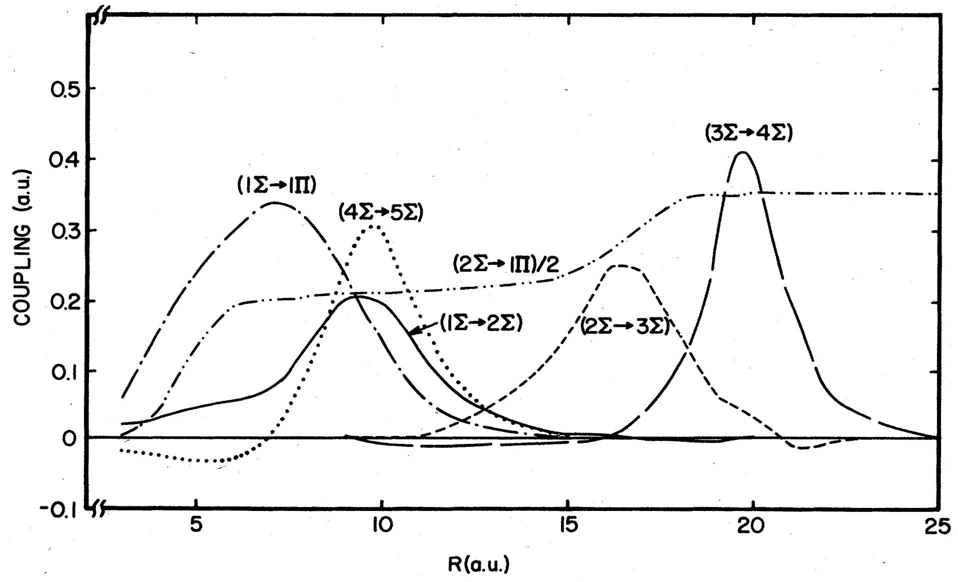

FIG. 2. A selected subset of the radial and rotational coupling matrix elements used in the scattering calculations.

TABLE IV. Cross sections in units of 10^{-16} cm^2 for production of neutral levels in the ion-ion mutual neutralization reaction.

State	0.1 keV/amu	1.0 keV/amu	10.0 keV/amu
$H + Cs(6s)$	12.5	7.48	2.63
$H + Cs^*(6p)$	35.4	22.5	9.82
$H + Cs^*(5d)$	76.5	18.2	4.21

method to determine the ion-pair formation cross section that could give rise to large cross sections at low energies due to elastic scattering of the beam.

Due to our favorable comparison to spectroscopic data[6] at the energy splitting of the critical $1\,^1\Sigma - 2\,^1\Sigma$ avoided curve crossing, Table III, we feel our molecular wave functions have sufficient accuracy to determine the cross section with an accuracy of ±25% at $E \leq 1$ keV/amu. At higher energies our confidence in the cross sections drops to ±50% due to our approximation to include only first-order terms in the electron-translation-factor correction and because there is increased competition from high-lying states and ionization channels.

The ion-pair formation cross section from the excited $H + Cs^*(6p)$ level, reaction (2), is larger than that from the ground state, Fig. 3. This effect is primarily due to the increased crossing radius, Table III. At the lowest energy evaluated by us, 100 eV/amu, there is an order-of-magnitude increase in the ion-pair formation cross section for collisions of H atoms with excited $Cs^*(6p)$ versus the ground state, $Cs(6s)$. Landau-Zener arguments can be used to explain this difference as due to the difference in the crossing radii and the potential-energy splittings at the avoided curve crossings. Our confidence level for this cross section is at the ±50% level and is primarily due to the decreased accuracy in describing the excited molecular levels of $H + Cs^*$.

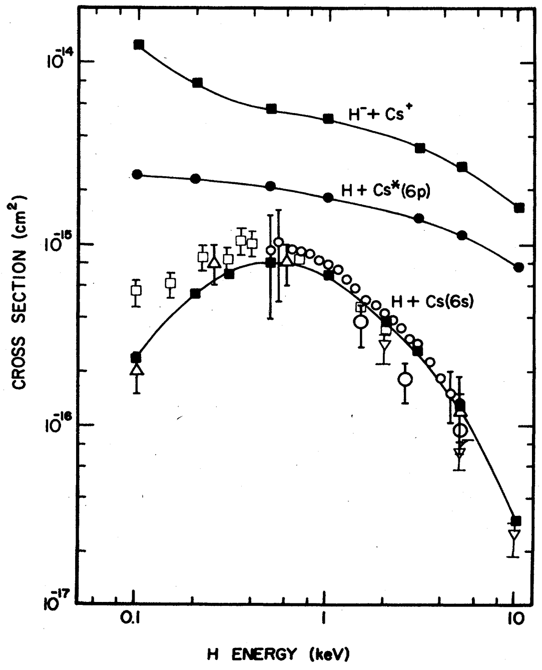

FIG. 3. Cross sections for the CsH system, reactions (1)—(3). The calculated points are given by solid symbols with a line drawn through them to aid the eye. Experimental data exist for the $H + Cs(6s) \rightarrow H^- + Cs^+$ reaction and are denoted by open triangles—Miethe *et al.* (Ref. 3), open squares—Meyer (Ref. 1), small open circles—Nagata (Ref. 2), large open circles—Schlachter *et al.* (Ref. 4), and open inverted triangles—Schlachter *et al.* (Ref. 5).

The ion-ion mutual neutralization cross section for reaction (3) is also shown in Fig. 3. This cross section is critical for the determination of the maximum H^- yields that can be extracted from high-current ion sources which use cesium-metal vapor. Excess Cs^+ in the cell will cause the H^- to be neutralized before it can be extracted. As expected from work on other systems,[20] the cross section is large and will exceed 10^{-14} cm^2 at low energies. The increase at low energies is due to the focusing effect of the attractive Coulomb potential between the reactants. At very low energies, $E \lesssim 1$ eV, the cross section becomes proportional to $1/E$.

To illustrate the fact that one cannot determine the ion-ion mutual neutralization cross section from the knowledge of the ion-pair formation cross section from the ground state, in Table IV we give product state distributions for reaction (3). At low energies the states with outer crossings are preferentially populated. As the energy is increased, the lower-lying states increase their contribution to the cross section. Our estimate of the accuracy of the calculated ion-ion mutual neutralization cross section is ±50%, due to our relative uncertainty of the accuracy of the high-lying molecular states. No experimental data exist to check the theoretical results.

CONCLUDING REMARKS

The pseudopotential method has been used to generate accurate interaction energies and wave functions for the CsH system. Coupled-channel scattering calculations have been performed in the energy range from 0.1 to 10.0 keV/amu to obtain the ion-pair formation cross sections from collisions of $H + Cs(6s)$ and $H + Cs^*(6p)$, and the ion-ion mutual neutralization cross section for $H^- + Cs^+$ collisions.

For $H + Cs(6s)$ collisions, the calculated cross sections are in accord with experimental measurements. This favorable comparison gives us confidence that the calculational results for $H + Cs^*(6p)$ and $H^- + Cs^+$ are reasonable. Of special interest is that the excitation of cesium to its resonance state, $Cs^*(6p)$, leads to a considerable enhancement of the ion-pair formation cross section at low energies, $E \lesssim 200$ eV/amu. Also, the ion-ion mutual neutralization cross section is quite large, a fact that may limit the formation of H^- in many high-current ion sources.

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[*] Permanent address: Department of Physics, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112, Japan.

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