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

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Pseudopotential molecular-structure calculations have been performed on the NaH system to obtain the five lowest $^1\Sigma$ and two lowest $^1\Pi$ molecular states. The resulting eigenfunctions and eigenvalues were used in a perturbed-stationary-state calculation where electron-translation factors have been incorporated to first order in the collision velocity. The ion-pair formation cross section for $H+Na \rightarrow H^- + Na^+$ is found to have a maximum value of 3.3×10^{-16} cm at 1 keV/amu. The ion-ion mutual neutralization cross section for $H^- + Na^+ \rightarrow H + Na$ rises monotomically with decreasing collision velocity and is $\sim 1\times10^{-14}$ cm^2 at energies from 0.1 to 5.0 keV/amu.

In a previous paper,[1] we reported cross-section studies on the $H+Cs \rightleftharpoons H^- + Cs^+$ system. To complement these studies and provide information as to trends in the alkali-metal systems, we have completed a similar investigation on the

$$H+Na \rightarrow H^- + Na^+ \quad (1)$$

ion-pair formation reaction, and the

$$H^- + Na^+ \rightarrow H + Na \quad (2)$$

ion-ion mutual neutralization reaction. Further motivation for our work arises from the disagreement between two recent experimental studies[2,3] on the cross section for reaction (1).

The calculation procedure was similar to Ref. 1. An l-dependent pseudopotential[4] which incorporates core-polarization effects was utilized to represent the Na^+-ion core. A Slater-type-orbital basis set, given in Table I, was used in the molecular-structure calculations. The calculated Na-ionization energies for the $3s$, $3p$, $3d$, and $4s$ levels are within 0.01 eV for the spectroscopic values. The hydrogen basis set was taken from Stevens, Karo, and Hiskes[5] and includes diffuse $1s$ and $2p$ orbitals to help in the representation of the $H^- + Na^+$ ion-pair level. All possible single and double electron excitations were included in the structure calculations which gave rise to 129 configurations for the $^1\Sigma$ molecular states and 96 configurations for the $^1\Pi$ molecular states. The calculated potential energies are displayed in Fig. 1.

TABLE I. Slater-type-orbital basis set.

H	$1s$	1.218
		0.463
	$2s$	1.058
	$2p$	1.058
		0.309
Na	$2s$	0.790
	$3s$	2.487
		0.694
		0.372
	$3p$	0.721
		0.558
	$4s$	0.290
	$3d$	1.484
		0.337

Of importance for the scattering calculations is the accuracy of the calculated energy splittings at the avoided crossings in the $^1\Sigma$ manifold. In Table II a comparison of our values with those of other researchers is given. The comparison with a large configuration-interaction (CI) calculation[6] and a spectroscopic interpretation[7] is quite good with our values being within $\pm 5\%$ of these values.

The scattering calculations for reaction (1) included the four lowest $^1\Sigma$ and the two lowest $^1\Pi$ molecular states shown in Fig. 1. For the ion-ion mutual neutralization reaction, the second $^1\Pi$ state was deleted since it was necessary that the incident level be a $^1\Sigma$ state which was not artificially

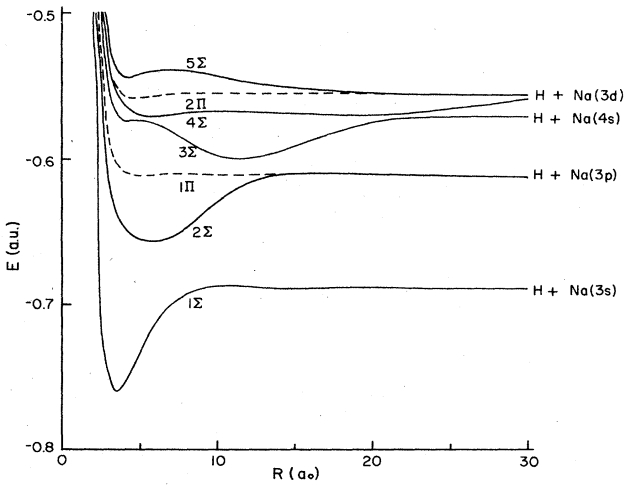

FIG. 1. Calculated singlet molecular states for the NaH system. The $^1\Sigma$ states are represented by the solid lines, while the $^1\Pi$ states are denoted by the dashed lines.

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

State	Reference	Method	$R_x(a_0)$	$V(R_x)$ (eV)
H+Na(3s)	This work	Pseudopotential	7.53	1.23
	Olson and Liu (Ref. 6)	CI	7.60	1.21
	Yang and Stwalley (Ref. 7)	Spectroscopic	7.71	1.18
H+Na(3p)	This work	Pseudopotential	13.08	0.427
	Olson and Liu (Ref. 6)	CI	13.28	0.407
	Janev and Radulovic (Ref. 8)	Asymptotic expansion	12.6	0.421
H+Na(4s)	This work	Pseudopotential	21.96	0.0690
	Janev and Radulovic (Ref. 8)	Asymptotic expansion	22.8	0.0435

mixed at large separations by a degenerate $^1\Pi$ state. All possible combinations of the radial and rotational terms were included in the cross-section evaluations. A representative set of coupling terms is displayed in Fig. 2. The radial matrix elements are peaked at the locations of the avoided curve crossings.

The perturbed-stationary-state coupled channel was used to determine the scattering amplitudes, and hence, the cross sections. Electron-translation factors were included to first order in velocity.[1] Straight-line classical trajectories were used for the nuclear motion.

The cross-section calculations for the ion-pair formation process, reaction (1), are shown in Fig. 3. The cross section rises to a maximum at 1 keV/amu. The calculated values are in good agreement with the experimental data of Howald *et al.*,[2] and lend credibility that these data are to be preferred over the previous meansurements of Nagata.[3] The coupled-channel Landau-Zener calculations of Janev and Radulovic[8] are also shown for comparison. Other measurements that will be published[9] further support our calculated values at energies $E < 1.0$ keV/amu.

Ion-pair formation was also investigated for the case where the Na atom is in its first excited state,

$$H+Na(3p) \rightarrow H^- + Na^+ \quad . \tag{3}$$

The cross section is greatly enhanced relative to collisions with ground-state atoms and is found to have an almost constant value of 1.0×10^{-15} cm^2 at energies from 0.1 to 1.0 keV/amu. The reason for the cross-section increase is readily understood by the larger value for the crossing radius to the ion-pair channel.

Ion-ion mutual neutralization, reaction (2), was also investigated. The calculational results are given in Fig. 4

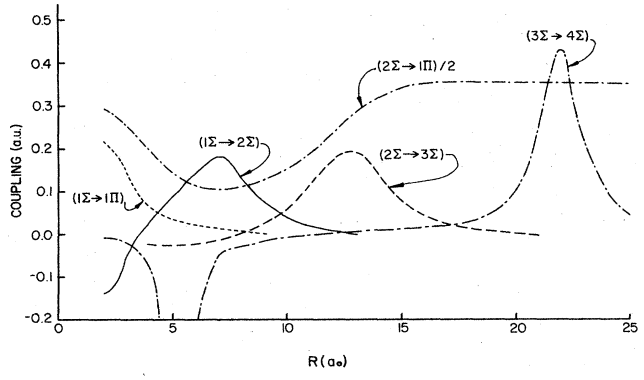

FIG. 2. A selected subset of the radial and rotational coupling matrix elements used in the scattering calculations.

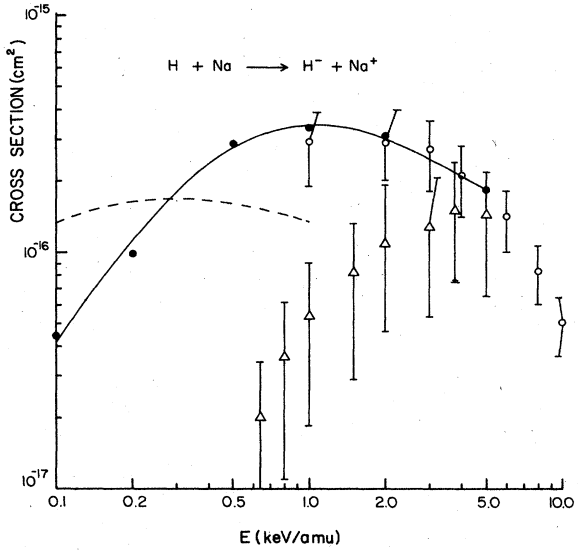

FIG. 3. Cross sections for the ion-pair formation process, reaction (1). Our calculated values are given by the solid points and the solid line. The calculated values of Janev and Radulovic (Ref. 8) are given by the dashed line. Experimental data of Howald *et al.* (Ref. 2) are denoted by open circles and the data by Nagata (Ref. 3) are shown as open triangles.

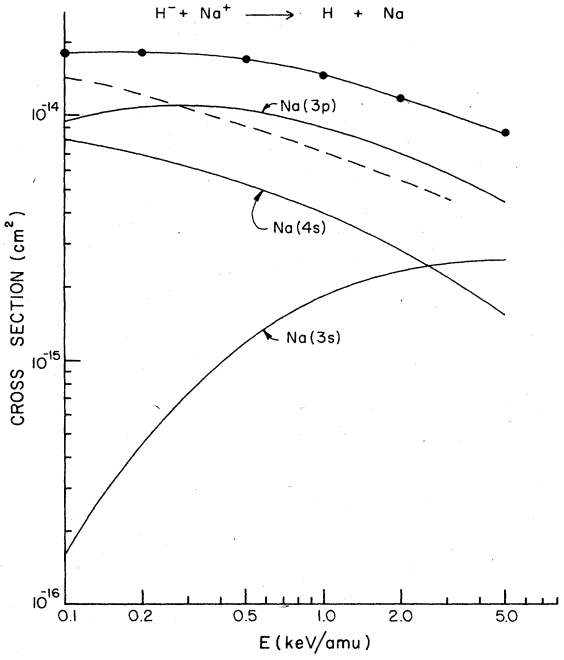

FIG. 4. Cross sections for the ion-ion mutual neutralization process, reaction (2). Our calculated values are given by solid lines with the overall total cross section being denoted by solid circles. The partial cross sections to the various product states, $H+Na^*$, are also given. The calculated total cross section of Janev and Radulovic (Ref. 8) is given by a dashed line.

along with the product states of the Na atom. The $H+Na(3p)$ level is preferentially populated at the energies studied. We did not include the $H+Na(3d)$ levels in the calculations since its crossing distance is at $\sim 35a_0$ and the coupling is expected to be weak. The partial cross section to $Na(3d)$ will be substantially less than $Na(4s)$ which has a crossing at $\sim 22a_0$. As expected, the trend in the partial cross section is to populate the low-lying levels with small crossing radii at high energies, and the high-lying levels with large crossing radii at the low energies. At very low energies, $E < 1$ eV, the attractive Coulomb initial channel determines the cross section which then increases as $1/E$ as the energy decreases. The $Na(3d)$ level is expected to become increasingly important as the energy is lowered.

In conclusion, coupled-channel calculations have been performed on the $H+Na \rightleftarrows H^- + Na^+$ reactions. Pseudopotential molecular-structure calculations were made to provide the eigenenergies and eigenfunctions for the scattering calculations. The calculated cross section for the ion-pair formation process, reaction (1), is in good agreement with the recent measurements of Howald *et al.*;[2] however, our values differ considerably from the experimental data of Nagata[3] and the Landau-Zener calculations of Janev and Radulovic.[8] The ion-ion mutual neutralization cross section, reaction (2), exceeds 1×10^{-14} cm^2 throughout most of the energy range investigated. The excited level $H+Na(3p)$ is the dominant product of the ion-ion reaction.

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