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Electron-capture collisions of H^+ with ground- and excited-state Na

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Pseudopotential molecular-structure calculations have been used to obtain the low-lying interaction energies for NaH^+ . The wave functions were used to calculate accurate radial and rotational coupling matrix elements. Scattering calculations which include electron translational factors were performed using up to eight coupled channels for laboratory energies 0.1 to 10 keV. Electron capture from ground-state Na $3s$ yields cross sections in the 10^{-15}-cm^2 range of which the dominant products are H $2s$ and H $2p$. Electron capture from excited Na $3p$ does not show an enhanced cross section relative to capture from the ground state even though the energy gap $\Delta E(R = \infty)$ to the dominant electron-capture channel is reduced from 1.74 to 0.36 eV.

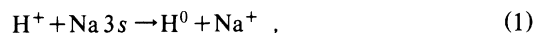
There has been considerable improvement in the quality and accuracy of calculated electron-capture cross sections in recent years. Fast computers have made it possible to perform numerical calculations with a sufficiently large number of molecular states to allow an accurate description of many scattering processes. Developments have been made also in the basic theoretical formulations, most notably on the inclusion of electron translational factors (ETF's). The use of ETF's removes the nonorthogonality between initial and final wave functions for electron-capture systems and allows for an accurate description of the cross sections to specific product states.

Recently, much theoretical effort has been placed on one-electron systems such as HeH^{2+} , where very accurate interaction energies and coupling matrix elements can be calculated. The inclusion of the effect of ETF's in the theoretical formulation has been explored by several groups.¹⁻⁴ However, to our knowledge, no molecular calculations have explored the effect of electron capture from both ground and excited electronic states.

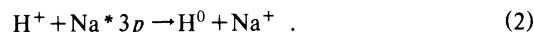
In order to benchmark the calculations against experiment, we have chosen to study alkali atom target systems because data are available. For these systems, the possibility exists to laser pump the resonance level of the alkali and to study excited-state reactions. Although more amenable experimentally, we must rely on less accurate wave functions to calculate the cross sections than in the true one-electron systems. However, the use of the pseudopotential method allows us to represent the alkali ion core with an analytical form which makes the calculations tractable and accurate if a suitably large basis set is utilized.

In this Communication we present interaction energies and electron-capture cross sections in the ener-

gy range of 0.1 to 10.0 keV for electron capture from the ground state



and from the excited state of Na,



Electron translational factors are incorporated in the calculations to remove spurious long-range coupling terms and to allow us to predict the cross sections to specific product states for reactions (1) and (2). Thus, besides providing a direct comparison between theoretical and measured cross sections for capture from the ground state, we are in a position to interpret the results of Kushawaha *et al.*⁵ for Lyman- α production in $H^+ + Na^*$ collisions. The sodium atom target system also provides a test of conventional arguments that electron-capture cross sections should increase if the target species is excited to a level which is more energetically resonant with the product electron-capture channels.

An l -dependent Gaussian pseudopotential of the form

$$V_p(r) = A_l \exp(-\zeta_l r^2) - \frac{\alpha_d}{2(r^2 + d^2)^2} - \frac{\alpha_q}{2(r^2 + d^2)^3} - \frac{1}{r} \quad (3)$$

was used to represent the Na^+ ion core. The parameters are taken from the work of Bardsley.⁶ Spin-orbit interactions were neglected and $1/R$ was used for the $H^+ + Na^+$ interaction. A molecular structure code developed by B. R. Junker was used to calculate the interaction energies.

A Slater-type orbital (STO) basis set was used for the wave-function expansion. The Na atom $2s$, $3s$,

and $3p$ optimized orbital exponents were from the work of Stevens *et al.*⁷ Two $3d$ and one $4s$ orbitals were added and the exponents optimized for the lowest energy of the representative Na atomic level. The hydrogen atom basis set is from the previous work of Olson *et al.*⁸ The energies of the H $1s$ and H ($n=2$) levels are exact, while the Na atom $3s$, $3p$, $4s$, and $3d$ energies are reproduced to better than 0.004 eV or 0.00015 hartree.

The entrance channel for the electron-capture calculations from the sodium atom ground state, the $A^2\Sigma^+$ molecular state, has been studied by several other groups. In Table I we compare our results using 18 basis functions to those of others for the equilibrium parameters R_e and D_e . Our calculations are in agreement with *ab initio* results⁸ for NaH^+ . As a test of basis set size, we have expanded the STO basis set to 29 functions which includes Na atom optimized $5s$, $4p$, $4d$, and $4f$ functions. The calculated equilibrium separation R_e for the $A^2\Sigma^+$ state was unchanged from the 18 basis functions result, but the dissociation energy D_e increased by 0.04 to 0.46 eV. The NaH^+ system appears adequately described for the scattering calculations. A graphical presentation of the interaction energies is given in Fig. 1.

The perturbed stationary states (PSS) method, modified to include ETF effects, has been used to calculate the detailed cross sections. In the framework of PSS theory, the time-dependent electronic wave function $\psi(\vec{r}, t)$ is expanded in terms of ETF modified Born-Oppenheimer (BO) wave functions

$$\psi(\vec{r}, t) = \sum_i a_i(t) \phi_i^{\text{BO}}(\vec{r}; \vec{R}) F_i(\vec{r}; \vec{R}), \quad (4)$$

where $F_i(\vec{r}; \vec{R})$ represents the ETF's and has a form

$$F_i(\vec{r}; \vec{R}) = \exp[(im/\hbar)^{1/2} f_i(\vec{r}; \vec{R}) \vec{V} \cdot \vec{r}]$$

and $f_i(\vec{r}; \vec{R})$ is a switching function^{11,12} as introduced by Schneiderman and Russek.¹³ The Born-Oppenheimer wave function ϕ_i^{BO} is the eigenfunction of the electronic Hamiltonian $H_{el} \phi_i^{\text{BO}} = E_i(R) \phi_i^{\text{BO}}$.

Substituting $\psi(\vec{r}, t)$ into the time-dependent Schrödinger equation and multiplying $\phi_j^* F_j^*$ from the

TABLE I. Potential-well parameters for the $A^2\Sigma^+$ state of NaH^+ .

Authors	Method	$R_e(a_0)$	$D_e(\text{eV})$
This work	Pseudopotential	7.89	0.42
This work	Pseudopotential (29 terms)	7.87	0.46
Reference 8	<i>Ab initio</i>	7.98 ± 0.1	0.47 ± 0.05
Reference 9	Pseudopotential	8.2	0.34
Reference 10	Model Potential	8.7	0.39

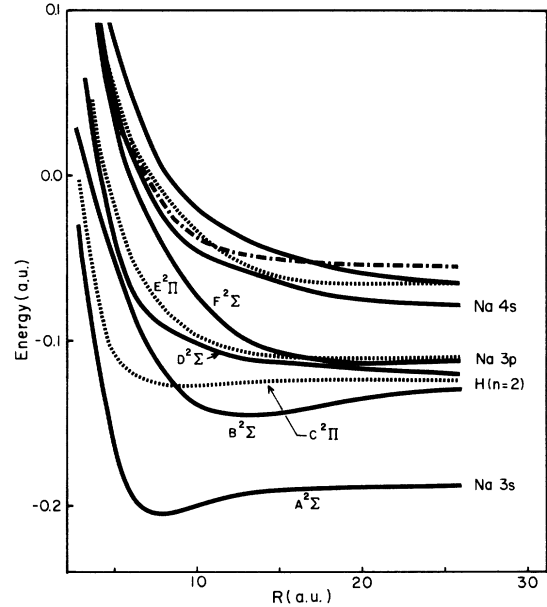


FIG. 1. Interaction energies calculated for the NaH^+ system. The $^2\Sigma^+$ molecular states are denoted by lines, the $^2\Pi$ states by dotted lines, and the $^2\Delta$ state by dash-dots.

left, and retaining the first-order terms of the relative nuclear velocity $\vec{V} = d\vec{R}/dt$, one obtains

$$\dot{a}_j = \sum_i \vec{V} \cdot (\underline{P} + \underline{A}) a_i \exp\left\{ \frac{i}{\hbar} \int^t (E_j - E_i) dt' \right\}, \quad (5)$$

where \underline{P} denotes the nonadiabatic coupling, involving both radial and rotational (angular) couplings and \underline{A} is the correction term to the nonadiabatic coupling due to the inclusion of the ETF's. From tests on systems such as $\text{H}^+ + \text{Na}$ where the coupling is well localized, the higher-order velocity corrections to Eq. (5) will decrease the cross section by no more than 5% at the highest energy studied, 10 keV.

Given the initial conditions $a_i(-\infty)$, the coupled Eqs. (5) are solved to obtain the transition probabilities by use of a classical description of the heavy particle motion. The coupled equations have been integrated numerically using the method of Bulirsch-Stoer,¹⁴ with the total absolute truncation error kept at the 10^{-4} – 10^{-6} level.

The calculated cross sections for electron capture from the Na $3s$ ground state, reaction (1), are given in Fig. 2. To test convergence, calculations at six energies from 0.1 to 10.0 keV were first performed with three states— $A^2\Sigma^+$, $B^2\Sigma^+$, $C^2\Pi$, four states—add $D^2\Sigma^+$, six states—add $X^2\Sigma^+$, and $F^2\Sigma^+$, and finally with eight states—add $E^2\Pi$ and the Na $4s^2\Sigma^+$ state. Convergence to better than 2% was realized with the four-state calculation for $E \leq 2$ keV, with this factor increasing to 13% at 10 keV. Electron capture into the H $2s$ and H $2p$ levels dominates the reaction with greater than 99% of the total cross section. Capture

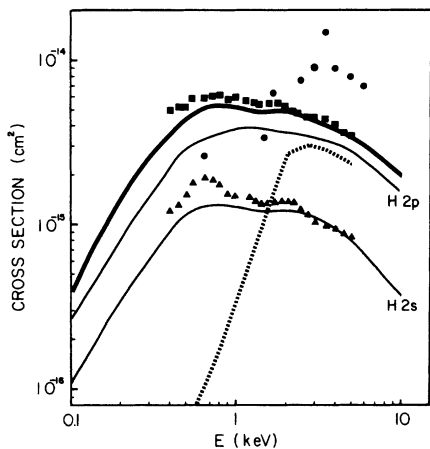


FIG. 2. Electron-capture cross sections for $H^+ + Na\ 3s$ collisions. Our calculations are denoted by solid lines. The H 2s and H 2p product cross sections are labeled. Experimental data of Nagata (Ref. 16) are given by solid squares for total electron capture and solid triangles for H 2s production. Data of Grüebler *et al.* (Ref. 17) are labeled by solid circles, and theoretical results of Kubach and Sidis (Ref. 10) are given by a dotted line.

to the ground state, the $X\ ^2\Sigma^+$ state of $Na^+ + H\ 1s$, is very small, with approximate cross sections of $2 \times 10^{-20}\text{ cm}^2$ at 0.1 keV, $3 \times 10^{-19}\text{ cm}^2$ at 1.0 keV, and $1 \times 10^{-18}\text{ cm}^2$ at 10 keV. The inclusion of curvilinear trajectories obtained from the use of the $A\ ^2\Sigma^+$ incident potential was made at 0.1 keV. The total cross section decreased 10% and was made up of 4% and 6% decreases in the H 2s and H 2p detailed cross sections. At higher energies, straight-line trajectories, as employed, are appropriate. The electron-capture process is the result of strong radial coupling between the $A\ ^2\Sigma^+$ and $B\ ^2\Sigma^+$ states which maximizes at $R \approx 12a_0$, and strong rotational coupling between the $A\ ^2\Sigma^+$ and $C\ ^2\Pi$ states at small R values. The oscillations in the cross sections are determined by a region of stationary phase caused by a maximum at $R \approx 5.5a_0$ in the difference potential¹⁵ between the $A\ ^2\Sigma^+$ and $B\ ^2\Sigma^+$ states.

As seen in Fig. 2, our calculated cross sections for total capture from the ground Na 3s state are in reasonable accord with the data of Nagata.¹⁶ The calculations disagree with the data of Grüebler *et al.*¹⁷ Kubach and Sidis¹⁰ have also performed electron-capture calculations from ground state Na 3s. These authors claim there is an experimental anomaly with Na atom targets and that all the experiments are incorrect. A more probable explanation is that the exceedingly small basis set employed in the molecular-structure calculations of Kubach and Sidis does not allow for an accurate description of the interaction energies and coupling terms, especially for $R \leq 10a_0$. The rotational coupling between the $A\ ^2\Sigma^+$ and $C\ ^2\Pi$ states at $R < 10a_0$ is an important

component to a theoretical description of this problem.

Also shown in Fig. 2 are the cross sections for production of metastable H 2s and H 2p which radiates to ground state H 1s with the emission of Lyman- α radiation. The H 2s cross section is in reasonable agreement with the experimental results of Nagata¹⁶ and displays a slight oscillatory behavior.

The calculated cross sections for electron capture from the excited $Na^*\ 3p$ target state are shown in Fig. 3. The cross sections are almost identical to those for capture from ground state Na 3s, whereas they were expected to be larger than from the ground state. Our reasoning relied on arguments that the energy gap $\Delta E(R = \infty)$ to the $H(n=2) + Na^+$ electron-capture channel decreases from 1.74 to 0.37 eV when the Na target is excited to the 3p state. Hindsight now indicates one must be very cognizant of the molecular structure, along with asymptotic energy separations, when making such predictions. From the $H^+ + Na^*\ 3p$ asymptotic limit, there arise $^2\Sigma^+$ and $^2\Pi$ molecular states with statistical weights of $\frac{1}{3}$ and $\frac{2}{3}$, respectively. The $F\ ^2\Sigma^+$ state couples strongly to the $D\ ^2\Sigma^+$ state of the $H(n=2) + Na^+$ electron-capture levels. However, the $E\ ^2\Pi$ state has very small coupling matrix elements to the $H(n=2) + Na^+$ electron-capture states and contributes very little to the total cross section. Hence, approximately $\frac{2}{3}$ of the incident flux is not available for the electron-capture process.

The cross sections for production of H 2s and H 2p from excited $Na^*\ 3p$ are also given in Fig. 3. They are almost identical to those for electron capture from the ground state (Fig. 2). Thus the ratio of Lyman- α production, after capture from ground- and excited-state Na, is approximately unity over the energy range studied. Experimental results confirming

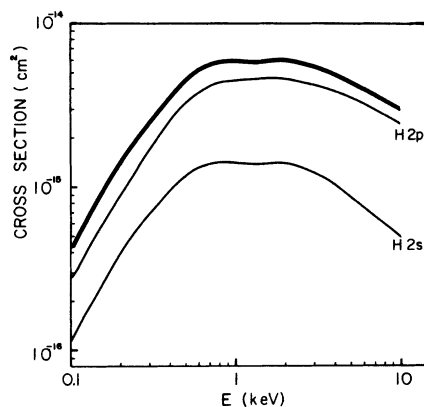


FIG. 3. Calculated electron-capture cross sections for $H^+ + Na^*\ 3p$ collisions. The heavy line indicates the total electron-capture cross sections. The H 2s and H 2p product cross sections are labeled.

this behavior have been presented by Kushawaha *et al.*⁵

In conclusion, we have presented cross-section calculations which include ETF's for a multielectron system. Cross sections to specific electron-capture product states are given for the interesting case of H⁺ colliding with Na in its ground and first excited levels. Recent experimental data by Nagata¹⁶ confirm our results and an interpretation of the observations of Kushawaha *et al.*⁵ is given.

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