

Electron detachment in low-energy $H^-(D^-)$ -Na collisions

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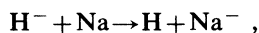
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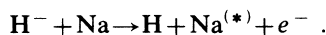
The contribution to electron detachment in low-energy $H^-(D^-)$ -Na collisions due to a direct transition from the bound ground state of $(HNa)^-$ to the $(HNa+e^-)$ continuum is studied in an effective-range approximation, based on *ab initio* calculations. Neutralization of H^- in collisions with Na atoms is shown to be dominated by this direct detachment process at low collision energies. At higher collision energies, charge transfer to $(H+Na^-)$ and detachment via charge transfer (previously studied by R. E. Olson and B. J. Liu [J. Chem. Phys. **73**, 2817 (1980)]) become the dominant H^- neutralization mechanisms. These theoretical results are compared with the experimental data of Y. Wang, R. L. Champion, and L. D. Doverspike [Phys. Rev. A **35**, 1503 (1987)]. A new calibration of these measurements is proposed, based on a comparison with previous absolute measurements at higher energies by A. M. Howald, L. W. Anderson, and C. C. Lin [Phys. Rev. A **24**, 44 (1981)].

I. INTRODUCTION

Recently, a few experimental studies^{1,2} were devoted to the study of low-energy H^- -Na collisions. The two main reactions leading to the neutralization of the H^- ion are charge transfer,



and electron detachment,



The second process can possibly be accompanied by excitation of the sodium target.

The salient features of the experimental results are the following. At the lowest collision energies that were studied,² the main process is electron detachment with cross sections decreasing to a few \AA^2 at 5 eV. As the collision energy is increased, the charge-transfer process becomes increasingly important, becoming comparable to the detachment process around 100 eV. At higher energies, the importance of the charge-transfer process decreases. Above a few hundred eV, the excitation of the sodium atom accompanying the detachment process becomes appreciable.¹ On the theoretical side, the results are more scarce. Karo *et al.*³ performed a multiconfiguration self-consistent field (MC SCF) calculation of the potential-energy curves for the ground state of HNa and $(HNa)^-$. The calculations indicated that the negative ion state is electronically stable at large internuclear separations and crosses into the $HNa+e^-$ continuum below $3a_0$. Olson and Liu⁴ performed a more detailed calculation; Fig. 1 presents their results for the two lowest-lying $(HNa)^-$ states correlating at infinity to $H + Na^-$ and $H^- + Na$.

They also reported on theoretical calculations of the charge-transfer and detachment processes at low collision energy which were not in complete agreement with the experimental results.² In particular, the theory underestimated the importance of electron detachment at low energies. These discrepancies have been discussed by Tuan and Esaulov¹ and Wang *et al.*² The aim of the present paper is to reexamine the problem of electron detachment in low energy H^- -Na collisions in order to try to further reconcile theory and experiment.

Figure 1 can be used to discuss the various mechanisms leading to the neutralization of H^- in collisions with

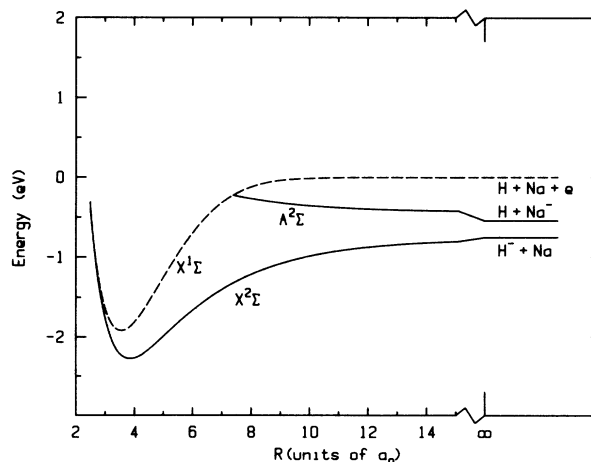


FIG. 1. Potential-energy curves for the low-lying states of NaH^- (solid lines) and for the ground state of NaH (dashed line) (Ref. 4).

sodium. Transitions which occur between H⁻-Na and H-Na⁻ at large internuclear distances leading to the charge transfer have been investigated by Olson and Liu.⁴ The upper negative ion state ($A^2\Sigma$) crosses into the (HNa+ e^-) continuum around $7.4a_0$ thus leading to one possible detachment mechanism involving a two-step process; viz., charge transfer from $X^2\Sigma$ to $A^2\Sigma$, followed by autodetachment in the (HNa+ e^-) continuum [detachment via charge transfer (DCT)]. This two-step mechanism is the detachment process studied by Olson and Liu.⁴ They evaluated the corresponding cross sections with the assumption that the autodetachment probability was unity at the $A^2\Sigma$ - $X^1\Sigma$ crossing.

The curves in Fig. 1 suggest an additional detachment mechanism: the potential-energy curve of the ground state of the negative ion is seen to cross into the (HNa+ e^-) continuum. This crossing is mentioned explicitly in Karo *et al.*,³ and its existence can be deduced from the tables in Olson and Liu.⁴ This second detachment mechanism involves a transition from the incident $X^2\Sigma$ state into the (HNa+ e^-) continuum and will be referred to as direct detachment (DD). In an independent electron representation, the electronic wave functions for the $X^2\Sigma$ incident state and for the (HNa+ e^-) continuum differ only by one orbital. Hence, the coupling in DD involves a one-electron term and thus can be anticipated to be large. Moreover, one can expect detachment to occur before the negative ion state crosses into the continuum via a direct transition from the bound state to low-lying continuum states. Such a transition is induced by the nuclear motion as has been discussed for H⁻-rare-gas systems.^{5,6}

In the following, we present a theoretical study of this direct detachment process for H⁻(D⁻)-Na collisions for collision energies in the 3–200-eV range. These results together with the previous results by Olson and Liu⁴ for charge transfer and detachment via charge transfer are compared with the experimental data of Wang *et al.*² In their original paper Wang *et al.* normalized their experimental results to the calculations of Olson and Liu. The validity of this normalization procedure is critically discussed below and a new calibration based on the absolute experimental results of Howald *et al.*⁷ is proposed.

II. METHOD

Because of the low relative velocity of the collision partners, the collision can be described by a molecular representation, i.e., one may study the evolution of a (HNa)⁻ molecular ion when the internuclear distance varies; because of the nuclear motion, this ion is not stable and can decay by electron emission. The nuclear motion is assumed to be classical and the time variation of the internuclear distance can be determined from a classical trajectory calculation. The description of the electron-HNa neutral molecule interaction utilizes the effective range approximation⁸ (ERA). This method is an extension of the zero range potential (ZRP) approximation⁹ which is used to handle arbitrary long-range electron-molecule interactions. The ERA was developed for studying vibrational and rotational excitation as well

as dissociative attachment in electron-molecule collisions^{10,11} and was recently extended to studies of electronic excitation in electron-molecule collisions.¹² The method is briefly outlined below. It consists of considering two different representations in two different regions of space and in matching them on the boundary. When the electron is far from the molecule, it is under the influence of a long-range local potential, $V_{LR}(r)$. As the electron penetrates into the molecule, the problem is more complicated. However, since the potential in this inner region is much larger than the asymptotic energy of the electron, the collision problem can be assumed to be energy independent in the inner region. The problem then reduces to solving the Schrödinger equation in the outer region with the logarithmic derivative specified on the boundary:

$$H = \frac{1}{2}\Delta + V_{LR}(r), \quad \frac{1}{\psi} \frac{\partial \psi}{\partial r} = f(R)$$

where ψ is the electronic wave function and R is the internuclear distance. The boundary condition f is a function of the internuclear distance of the HNa core; its R dependence, transformed into a time dependence by the classical trajectory approximation, induces the detachment process. The (HNa) molecule is dipolar, and the long-range potential V_{LR} is chosen to be dipolar. The Schrödinger equation for an electron in a dipolar potential is separable in angular and radial coordinates, thus defining the dipolar angular modes.¹³ The ground state of the (HNa)⁻ ion corresponds to the lowest dipolar angular mode, which correlates to an s wave in the limit of a vanishing dipole moment. Since the rotational coupling between the (HNa)⁻ ground state and $^2\Pi$ (HNa+ e^-) continua is expected to be small, one may assume as a further approximation that only one angular mode is active in the collision. The angular part of the electron wave function during the collision will then be the lowest dipolar angular mode. For the radial motion of the electron, the long-range potential reduces to the radial dipole potential:

$$V_{LR} = -\frac{A}{2r^2}, \quad (1)$$

where A , the separation constant, depends on the strength of the dipole. Based on the above approximation, the collision problem reduces to solving the time-dependent, radial electron wave function ψ in the outer region which is described by

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial r^2} - \frac{A}{2r^2} \right] \psi = i\hbar \frac{\partial \psi}{\partial t}, \quad (2)$$

$$\frac{1}{\psi} \frac{\partial \psi}{\partial r} \Big|_{r_0} = f(t). \quad (3)$$

The electron radial coordinate r_0 corresponds to the boundary between the inner and outer regions defined by the ERA. It must be small enough that the potential in the inner region is significantly larger than the absolute value of the energy of the outer electron (bound or free). In the present calculations r_0 was set to $3a_0$.

These equations are an extension of the similar ones derived in the ZRP approximation, in the absence of a long-range potential^{5,8} and can be solved in the same way by a direct numerical integration.⁵ Basically, this method consists of representing the wave function $\psi(r,t)$ by its values on a discrete set of equally spaced points, $\psi(r_i,t_j)$, and in propagating it by means of the Schrödinger equation (2). The integration begins with ψ being the $(\text{HNa})^-$ bound state; at the end of the collision ψ is projected on this bound state to yield the survival probability (for more details, see Ref. 5).

The main input for the above calculation is the boundary condition on the logarithmic derivative f of the wave function which is a function of the internuclear distance; $f(R)$ can easily be obtained from the knowledge of the outer electron binding energy in $(\text{HNa})^-$. Indeed, for the fixed R problem, f is simply the logarithmic derivative of the bound outer-electron wave function on the boundary. It can be obtained from the numerical integration for $r \geq r_0$ of the Schrödinger equation:

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial r^2} - \frac{A}{2r^2} + \varepsilon(R) \right] \psi = 0,$$

where $\varepsilon(R)$ is the outer-electron binding energy in $(\text{HNa})^-$ and ψ is a pure outgoing wave at infinity. The results of Karo *et al.*³ for $\varepsilon(R)$ were used in the present study. To correct for the slight inaccuracy of the electron binding energy at infinity (0.664 eV instead of 0.754 eV, the hydrogen electron affinity) the $(\text{HNa})^-$ potential-energy curve was shifted by 90 meV with respect to the (HNa) ground-state potential. These results for $\varepsilon(R)$ were available only for $R \geq 3a_0$, precluding values for f below $3a_0$. However, since f is a molecular quantity, it should not exhibit any drastic variation with R as long as the neutral molecular state does not vary rapidly with R ; it can then be extrapolated rather safely into the region where no *ab initio* results are available.

The dipole potential felt by the electron was taken to be independent of R with a dipole moment of 5.3 D (separation constant $A = 1.81$ a.u.). To confirm the validity of the above, a few test calculations were performed assuming A is a function of R . Results very similar to the present ones presented below for constant A were obtained. (The R dependence of the dipole was taken from Ref. 14.) In the same way, various extrapolations of the boundary condition for $R < 3a_0$ were examined and found to have little effect on the final results. A few test calculations were also performed in the ZRP approximation, i.e., without taking into account the HNa dipolar potential. The ZRP boundary condition f_{ZRP} was determined from the binding energy of the $(\text{HNa})^-$ ion; its extrapolation to small R corresponds to the transformation of the bound state into a virtual state. These test ZRP calculations yielded detachment probabilities qualitatively similar to the present ERA results, however, significantly smaller, thus showing the influence of the long-range dipolar potential. The presence of a long-range dipolar potential indeed modifies the wave function of the bound electron. In the ZRP approximation, the outer region is classically forbidden and the ZRP wave

function is a decreasing exponential. In the ERA, because of the attractive potential, there exists a larger classically allowed region; for example, the classical turning point for the outer electron is around $11a_0$ for a binding energy of 0.2 eV. The electron wave function is then much more diffuse in the ERA than in the ZRP approximation, and this could be linked with the different detachment probabilities obtained in the two approaches.

An interesting property of the point dipole potential is its ability to support a bound electronic state if the dipole moment exceeds 1.62 D.¹³ For a dipole of 5.3 D, there always exists a bound state, independent of the boundary condition at r_0 . In the present ERA calculation with a constant dipole moment, the extrapolation of $f(R)$ below $3a_0$ yields a decreasing binding energy as shown in Fig. 2, saturating around 30 meV. In a calculation with an R -dependent dipole, the binding energy as well as the dipole moment decreases as R decreases and eventually the binding energy vanishes when the dipole becomes subcritical. These features are not present in the calculations of Olson and Liu,⁴ or Karo *et al.*³ owing to the very low binding energy expected at small internuclear distances, which would require an expansion over very diffuse orbitals to be properly described. Different choices in the ERA parametrization (constant or variable dipole, value of the dipole) indeed leads to different binding energies at small internuclear distances. However, during the collision, the system does not adiabatically follow these loosely bound states, leading to electron ejection into the continuum rather early in the collision. This accounts for the weak dependence of the final result on the detailed features of the dipole. Another aspect of strong dipolar fields is that they possess an infinite number of bound states,¹⁵ the binding energies of which rapidly decrease. For example, in the present case, at $R = 3.0a_0$ and $A = 1.81$ a.u., the ground state of $(\text{HNa})^-$ is bound by 0.116 eV, whereas the second state is only bound by 7.5×10^{-4} eV. Although these bound states are implicit-

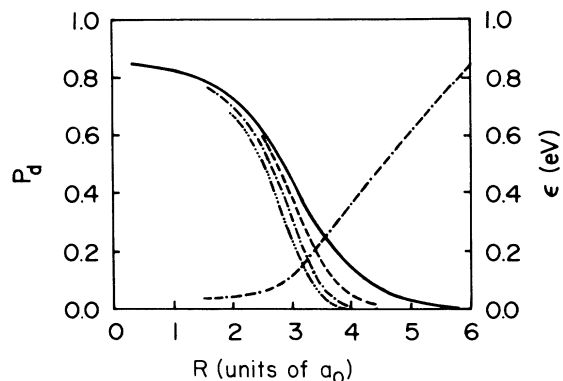


FIG. 2. Direct detachment probabilities (left scale) for H^- - Na collisions at various center-of-mass energies as functions of the turning point of the classical trajectory (—, 200 eV; ---, 30 eV; - · - · -, 9 eV; · · · · -, 4 eV). The binding energy of the HNa^- ground state (right scale) is shown (- · - · -) as a function of the internuclear distance.

ly taken into account by the collision treatment, they will not be considered below because of their very low binding energy; the nuclear motion will very efficiently destroy them and they will contribute to the detachment process.

III. RESULTS AND DISCUSSION

Figure 2 presents the detachment probability for H⁻-Na collisions calculated for four different center of mass energies: 4, 9, 30, and 200 eV. They are presented as functions of the turning point of the trajectory R_0 rather than as a function of the impact parameter. Collisions having the same turning point R_0 but different velocities experience the same coupling regions, and thus $P_d(R_0, E)$ is representative of the velocity effects¹⁶ in the collision process. In the present calculations, the ground state of (HNa)⁻ does not penetrate into the continuum; an adiabatic behavior would then correspond to a vanishing detachment probability. However, due to the nuclear motion, the electron is ejected into the continuum with probabilities up to 85%, even at the lowest velocities. From Fig. 2 one can see that binding energies (ϵ) as high as 0.2–0.4 eV nevertheless yield transition probabilities around 10%. As further evidence of the dynamical character of this detachment process, the detachment probability at fixed R_0 is seen to increase with the collision velocity. The characteristics of this detachment process are then very similar to that of the H⁻-Ne system, where the negative ion state is bound for all internuclear distances.^{6,17} The calculations have been performed for both H⁻ and D⁻ projectiles at low collision energies (3 eV < E < 200 eV), corresponding to the domain studied by Wang *et al.*² Since the calculations involve classical motion of the nuclei, they cannot be extended to very low collision energies and were restricted to collision energies above 3 eV. For collision energies above a few hundred eV, Tuan and Esaulov¹ observed excitation of the sodium target. The present calculations which only deal with the lowest-lying states cannot treat these excitation processes and consequently the calculations were restricted to collision energies below 200 eV, where the effect of excitation channels could be neglected.

For the detachment process, two different mechanisms have to be considered. Direct detachment, as determined from detachment probabilities as given in Fig. 2, is the dominant detachment process at low collision energies. As may be seen in Fig. 3, the cross section for direct detachment σ_{DD} increases from 5.5 Å² to 8 Å² in the energy range 3–200 eV; this increase is related to the dynamical character of DD. The additional mechanism of detachment via charge transfer σ_{DCT} was studied by Olson and Liu. The DD and DCT cross sections were computed independently and one should take into account the effect of one on the other. The total detachment was thus evaluated in the following manner:

$$\sigma_{\text{tot}} = \sigma_{DD}x(1 - P_{\text{tr}}) + \sigma_{DCT}, \quad (4)$$

where σ_{DD} and σ_{DCT} are the cross sections for each process treated alone and P_{tr} is the transition probability for charge transfer at large distances. For this probability we

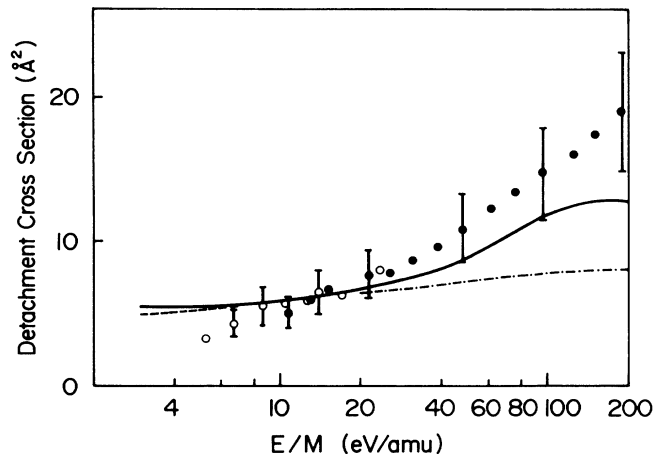


FIG. 3. Total cross section for electron detachment in H⁻(D⁻)-Na collisions as a function of E/M (relative collision energy/reduced mass). The dots are the experimental results of Wang *et al.* (Ref. 2; open symbols, D⁻ projectile; closed symbols, H⁻ projectile). The solid line is the σ_{tot} , given by Eq. (4), for H⁻. The dot-dash line is the contribution from the direct detachment. The dashed line for $E/M < 8$ eV/amu is for the detachment of D⁻ which differs from the H⁻ results only at low values of E/M .

used the Demkov formula.¹⁸ The effect of this corrective factor ($\sigma_{DD}P_{\text{tr}}$) is quite small for $E < 80$ eV and amounts at most to 1 Å² for $E = 200$ eV. The detachment cross sections so calculated are given in Fig. 3. A calculation of σ_{DCT} has also been presented by Wang *et al.* A reexamination of those calculations, by expressing them in the proper molecular basis, leads to cross sections that are consistent with Olson and Liu's results for σ_{DCT} , within the expected accuracy of the perturbation treatment.

The charge-transfer cross section as calculated by Olson and Liu was similarly modified to take into account the loss of flux due to direct detachment. Figure 4 presents the following charge-transfer cross section:

$$\sigma'_{\text{CT}} = \sigma_{\text{CT}} - \sigma_{DD}P_{\text{tr}}(1 - P_{\text{tr}}), \quad (5)$$

where σ_{CT} is the charge-transfer cross section as computed by Olson and Liu.

The previous data of Wang *et al.* were relative and their normalization was achieved by comparison with σ_{CT} computed by Olson and Liu.⁴ This normalization was somewhat ambiguous as the calculated and measured charge-transfer cross sections have different slopes, and as the theoretical detachment cross section obtained in the same calculation did not agree with the experimental cross section. An alternative normalization may be obtained from a comparison with the absolute measurements of Howald *et al.*⁷ for the total electron-loss cross section at higher collision energies. Such a normalization is presented in Fig. 5 which shows both the data of Howald *et al.*⁷ and the renormalized data of Wang *et al.* Although the two energy ranges do not overlap, the normalization was chosen such that the extrapolations of the

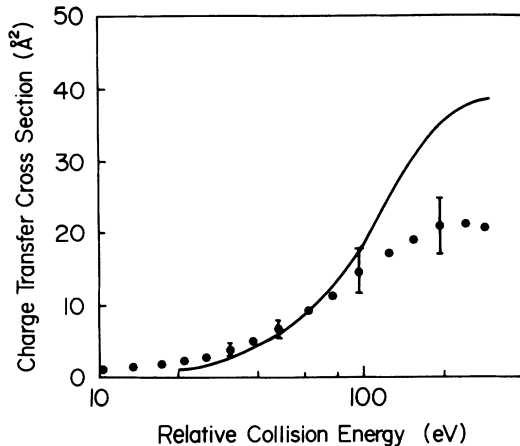


FIG. 4. Total cross section for charge transfer in H^- -Na collisions as a function of collision energy. The dots are from Wang *et al.* (Ref. 2) and the solid line is from Eq. (5), based upon the calculation of Olson and Liu (Ref. 4).

two sets of data match. The new normalization, which corresponds to dividing the Wang *et al.* published cross sections by a factor 1.6, is believed to be an improvement over the previous one.

The data, so normalized, are compared in Figs. 3 and 4 with theoretical results already discussed. The present calculations were made for both H^- and D^- projectiles. The D^- results are also presented on Fig. 3, for comparable collision velocities (i.e., the cross sections are displayed as a function of E/M). The D^- and H^- detachment cross sections are very similar, except at low energy ($E_H < 8$ eV) where the D^- cross section is slightly smaller than that for H^- . The calculations were not performed below 3 eV due to the expected breakdown of the classical trajectory approximation. However, the total detachment cross sections can be expected to increase at smaller collision velocities (v) and to exhibit a Langevin (orbiting) type of behavior where $\sigma_{DD} \approx 1/v$. The agreement between theory and experiment is reasonable for the lowest energies, but diverges at higher energies. From Figs. 3 and 4, one can see that the theory overestimates the charge transfer and underestimates the detachment cross section. However, for the total neutralization cross section (Fig. 5), the agreement is reasonable, and the theoretical curve lies within the experimental error bars. A possible cause of the discrepancies at high energies in Figs. 3 and 4 then lies in the partitioning between the charge transfer and the detachment via the charge-transfer process. An increase of the crossing radius between the ionic $A^2\Sigma$ and the neutral $X^1\Sigma$ potential-energy curves would indeed improve the agreement between theory and experiment. The inclusion of dynamical effects for DCT (direct jumps from the bound $A^2\Sigma$ to the continuum before the crossing point) would also tend to reduce the discrepancy.

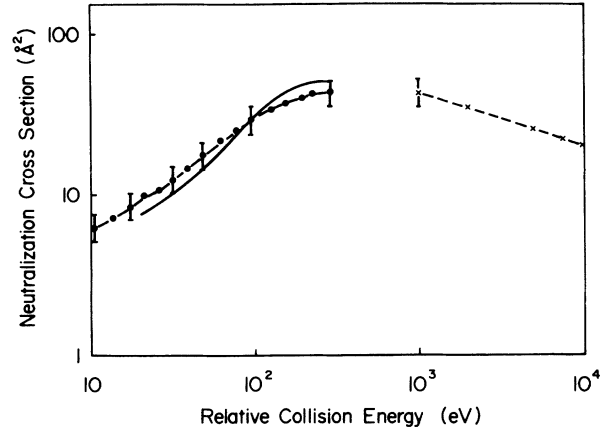


FIG. 5. Total cross section for the neutralization of H^- in H^- -Na collisions as a function of relative collision energy. The crosses are the experimental results of Howald *et al.* (Ref. 7). The dots are the renormalized results of Wang *et al.* (Ref. 2) for the sum of the detachment and charge-transfer cross sections. The solid line is the present theoretical result.

IV. SUMMARY

Direct detachment corresponding to a direct transition from the bound $(HNa)^-$ state to the $(HNa + e^-)$ continuum has been studied using an effective range approximation for the $(e^- - HNa)$ interaction based on *ab initio* results. Such a process does not exist in an adiabatic picture since the $(HNa)^-$ ground-state potential does not cross into the continuum. The process is then induced by the relative motion of the heavy particles. It has all the characteristics of a dynamical process, similar to the detachment process in the H^- -Ne system. Direct detachment is found to be the dominant process for H^- neutralization in H^- -Na collisions for $E \leq 40$ eV, whereas charge transfer (which may lead to detachment) is the most important process for the neutralization of H^- by atomic sodium at higher collision energies.

A new normalization of the experimental results of Wang *et al.*² has been proposed based on a comparison with previous experimental results at higher energies.

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