

An *ab initio* study of mutual neutralization in $\text{Na}^+ + \text{H}^-$ collisions

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Abstract. First principles calculations of mutual neutralization in $\text{Na}^+ + \text{H}^-$ collisions have been performed for collision energies between 0.01 and 100 eV. A ten-state molecular expansion has been employed with a quantal description of the relative motion and a diabatic *ab initio* calculation for the two active electrons. While results for the total neutralization cross section are generally within 15% of those obtained by Janev and Radulović (1978), cross sections into the less populated final states differ much more, by in excess of an order of magnitude for the 3p level. At 100 eV satisfactory agreement is obtained with the results of Olson and Kimura (1985). The low-temperature rate coefficient for mutual neutralization is calculated to be $3.0 \times 10^{-7} (T/300 \text{ K})^{-1/2} \text{ cm}^3 \text{ s}^{-1}$. Cross sections for ion-pair production in $\text{Na}(3l) + \text{H}$ collisions have also been determined, showing substantial differences from the results of Janev and Radulović (1978), particularly for production from 3s at low energy. Differences of 5% and 35% from the calculations of Olson and Kimura (1985) for 3s and 3p, respectively, at 100 eV are obtained.

1. Introduction

Mutual neutralization processes are important in a variety of cool plasma environments such as the interstellar medium (Millar *et al* 1997), the ionosphere (Smith and Adams 1983) and plasma etch reactors (Bartels 1995). Reactions involving specifically H^- are of interest in ion sources, particularly for neutral-beam injection for heating fusion plasmas (Bacal *et al* 1996). Collisions involving H^+ and H^- and Li^+ and H^- have been studied extensively, both experimentally (Szücs *et al* 1984, Peart and Hayton 1992, 1994 and references therein) and theoretically (Fussen and Kubach 1986, Croft *et al* 1999a and references therein). We have recently completed a theoretical study of the Li^+/D^- reaction, which gave agreement within 20% with merged-beam measurements of the absolute cross section at collision energies down to 0.68 eV (Croft *et al* 1999a). Here we extend that work on Li^+ to Na^+ . As well as their interest for collision studies, these processes at low energy provide a sensitive means of probing long-range ($\geq 20 a_0$) ionic–neutral interactions in regions not normally accessible to molecular spectroscopy.

Previous work on Na^+/H^- mutual neutralization has been performed by Janev and Radulović (1978), by Olson and Kimura (1985) and by Errea *et al* (1986). Janev and Radulović used the Landau–Zener approximation for energies between 0.01 eV and 10 keV with couplings determined by asymptotic methods. Olson and Kimura employed pseudopotential molecular structure calculations to determine the potentials and couplings and solved the perturbed-stationary-states coupled-channel equations with a straight-line path for the amplitudes for

energies between 0.1 and 5.0 keV u⁻¹. Errea *et al* used a five-state molecular expansion, again with a straight-line path, including translation factors, with potentials and couplings calculated using model-potential methods (Mó *et al* 1985) for energies between 0.16 and 5 keV u⁻¹.

Studies of Na excitation in slow collisions with hydrogen atoms (Fleck *et al* 1991, Mó and Riera (1992), Belyaev *et al* 1998 and references therein) involve both singlet and triplet NaH interactions. Of these, only the singlet interactions are relevant to mutual neutralization and comparison can be made with molecular potentials and couplings calculated for these studies (Olson and Liu 1980, Bruna and Pyrimhoff 1987, Belyaev *et al* 1999), although the primary interest is in lower-lying states than those dominant in mutual neutralization at low energy.

As with Li⁺/H⁻, since there are significant radial couplings present it is not anticipated that rotational couplings will play a major role in the total neutralization reaction. However, inclusion of rotational couplings would be important for determining magnetic substate populations in the final channels.

In section 2 we discuss our molecular potentials and couplings. The cross sections are discussed in section 3 and our conclusions are presented in section 4. Atomic units are employed unless otherwise stated.

2. *Ab initio* calculation

To employ the molecular expansion method (Macías and Riera 1982, Kimura and Lane 1990 and references therein) as used in our previous study (Croft *et al* 1999a) and used in other Na + H calculations (Olson and Kimura 1985, Errea *et al* 1986, Belyaev *et al* 1999), extensive *ab initio* calculations have been performed for the ¹Σ⁺ states of the NaH molecule. The detailed presentation of these calculations will be reported separately (Poteau and Gadéa 1999). We will concentrate here on the aspects relevant to neutralization, hence particularly on the neutral-ionic avoided crossings in this symmetry.

We followed an approach similar to that used for the LiH study (Boutalib and Gadéa 1992). Adiabatic results were obtained using an *l*-dependent pseudopotential for the Na core and the important core-valence correlation effects were estimated from an operatorial approach (Foucrault *et al* 1992), which involves *l*-dependent cutoff parameters optimized on the atomic spectrum. For the interaction between the polarizable Na⁺ core, the valence electrons and the H nucleus, an operatorial core polarization potential (CPP) is used (Müller *et al* 1984):

$$V_{\text{CPP}} = -\frac{1}{2} \sum_c \alpha_c \mathbf{f}_c \cdot \mathbf{f}_c \quad (1)$$

where α_c is the polarizability of the core *c* and \mathbf{f}_c is the electric field produced by the valence electrons and all other cores at the core *c*;

$$\mathbf{f}_c = \sum_i \frac{\mathbf{r}_{ci}}{r_{ci}^3} F_l(r_{ci}, \rho_c^l) - \sum_{c' \neq c} Z_{c'} \frac{\mathbf{R}_{c'c}}{R_{c'c}^3} \quad (2)$$

where $F_l(r_{ci}, \rho_c^l)$ represents the cutoff function and ρ_c^l the *l*-dependent cutoff parameters (Foucrault *et al* 1992). For Na a very large basis set was employed in order to describe almost all the electronic states which dissociate below the ionic limit, Na⁺ + H⁻. The basis set for H was selected in order to describe both the neutral (H(1s)) and the ionic (H⁻) configurations. Because of linear dependences at short internuclear separations some diffuse functions from the basis set for H employed in the LiH study were discarded.

As can be seen in table 1, accurate atomic values were obtained. Those for Na up to 4s are the most relevant for neutralization: they are accurate within a few cm⁻¹. The largest error is for the ionic limit, the electron affinity of H being underestimated here by 834 cm⁻¹.

Table 1. Atomic limits in cm^{-1} . EAH is the electron affinity of hydrogen.

Atomic State	Without core–valence correlation	With core–valence correlation	Experimental ^a	Error
Na(3s)	−39 968	−41 450	−41 450	0
Na(3p)	−24 020	−24 482	−24 482	0
Na(4s)	−15 408	−15 708	−15 710	2
Na(3d)	−12 216	−12 276	−12 277	1
Na(4p)	−11 047	−11 177	−11 179	2
Na(5s)	−8 133	−8 243	−8 249	6
Na(4d)	−6 858	−6 887	−6 901	14
Na(4f)	−6 834	−6 837	−6 861	24
Na(5p)	−6 340	−6 394	−6 408	14
Na^+	0	0	0	0
H(1s)	−109 596	−109 596	−109 737	141
EAH	5 249	5 249	6 083 ^b	834

^a Moore (1949).^b Hotop and Lineberger (1985).

This error can easily be corrected with the help of the diabatic representation, which is, moreover, the more convenient for the dynamics since we have only potential couplings, instead of the derivative couplings of the adiabatic representation. All ten $^1\Sigma^+$ states up to the ionic limit were included in the diabatic–adiabatic transformation, i.e. those dissociating to Na(3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p)H(1s) and to the ionic Na^+H^- .

The unitary transformation yielding the diabatic states from the adiabatic ones was derived following an approach proposed recently (Gad  a and Pelissier 1990). The method combines an effective overlap matrix between the atomic basis sets with variational effective Hamiltonian approaches (Gad  a 1991). The main idea underlying this approach is to perform a finite-difference estimate of the radial coupling and to cancel it (Gad  a and Pelissier 1990) using the properties of the variational formulation (Gad  a 1991) of the des Cloizeaux effective Hamiltonian.

$$H_{\text{diab}}^{\text{el}} = H_{\text{var}}^{\text{eff}} = (\Omega^\dagger \Omega)^{-\frac{1}{2}} \Omega^\dagger E_{\text{adia}} \Omega (\Omega^\dagger \Omega)^{-\frac{1}{2}} \quad (3)$$

$$\Omega = \langle \Psi^{\text{adia}}(R) | \Phi^{\text{ref}}(R + \Delta R) \rangle \quad (4)$$

where $\Psi^{\text{adia}}(R)$ denotes the adiabatic wavefunction at internuclear separation R and $E_{\text{adia}}(R)$ the corresponding adiabatic energy. The coupling matrix Ω corresponds to the overlap between two sets of functions, a set of adiabatic functions at separation R where the diabaticization is currently performed (forming the target space) and a set of known diabatic reference functions for another distance $R + \Delta R$ (forming the model space). This estimate uses quite large ($\approx 1 a_0$) intervals ΔR between neighbouring points, instead of the infinitesimal displacements which would be used in a conventional calculation. In the effective metric used for the calculation of Ω the diagonal blocks of the overlap matrix are replaced by their asymptotic limit. In this way a remarkable stability is obtained and the unitary transformation approaches the unit matrix at large separations. It may be noted that this estimate of the radial coupling is not singular and the effective metric ensures by construction vanishing couplings for large distances. Electron translation factors (ETF) (Errea *et al* 1994 and references therein) allow for dynamical cancellation of the asymptotic couplings. Here, some static substitute for the ETF is produced since, at large distances, where there is only translation of the basis sets but no real change in the electronic wavefunctions, the diabatic states are identical to the adiabatic ones. The origin dependence is related to the off-diagonal blocks of the effective metric. We

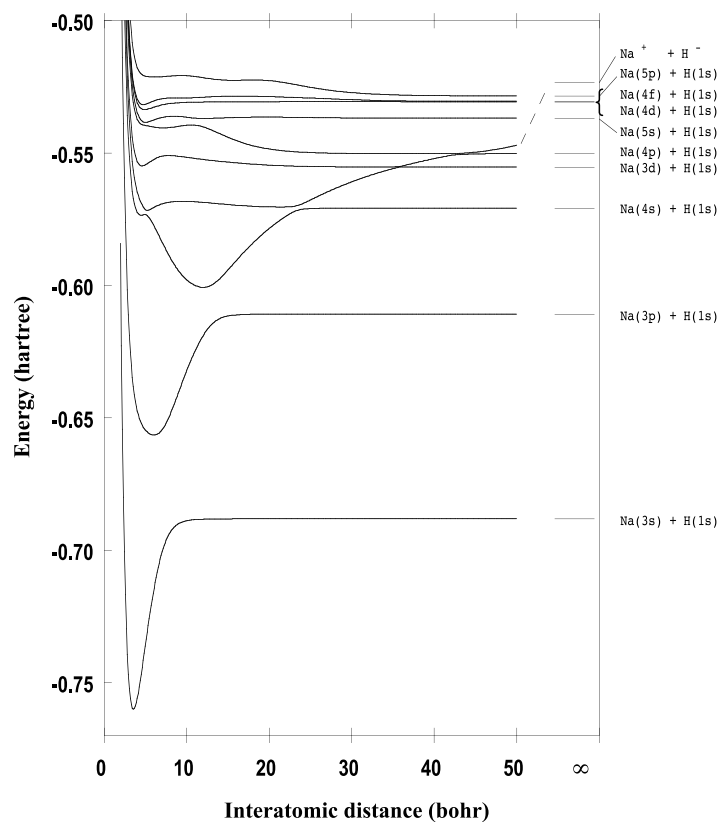


Figure 1. Adiabatic energies for the lowest ten $1\Sigma^+$ states of NaH.

fixed here, as for LiH, the origin in the heavier atom (Na). Asymptotically these terms vanish and globally we have a weak origin dependence.

In the practical implementation of the variational effective Hamiltonian at each distance the model space and target space need to be defined. The target space is unambiguously formed by the ten lowest adiabatic functions of the proper symmetry. For the model space, in contrast to the approach adopted for LiH where the space was formed by the asymptotic adiabatic functions, here we use the ten diabatic functions determined for the larger adjacent distance. This choice was motivated by a recent study on Na + Rb⁺ collisions (Romero *et al* 1999), which clearly showed the latter approach to be superior.

Adiabatic and diabatic functions have been determined over a grid of 166 points from $R = 2 a_0$ to $R = 316 a_0$. The ionic diabatic curve was corrected for the error in the hydrogen electron affinity. Although the correction introduces changes only in the diagonal term of the effective Hamiltonian corresponding to the ionic potential (which is lowered by an R -independent energy shift of 834 cm^{-1}), all other matrix elements remaining unaffected, the corrected effective Hamiltonian matrix can be diagonalized leading to improved adiabatic energies. Thus, this correction influences consistently the adiabatic and diabatic results. The main improvements occur when large ionic components are involved in the wavefunction, for example for the dissociation energy, D_e , of the ground state and for neutral–ionic avoided crossings. The corresponding potential curves are shown in figures 1 and 2 for the adiabatic and diabatic approaches, respectively.

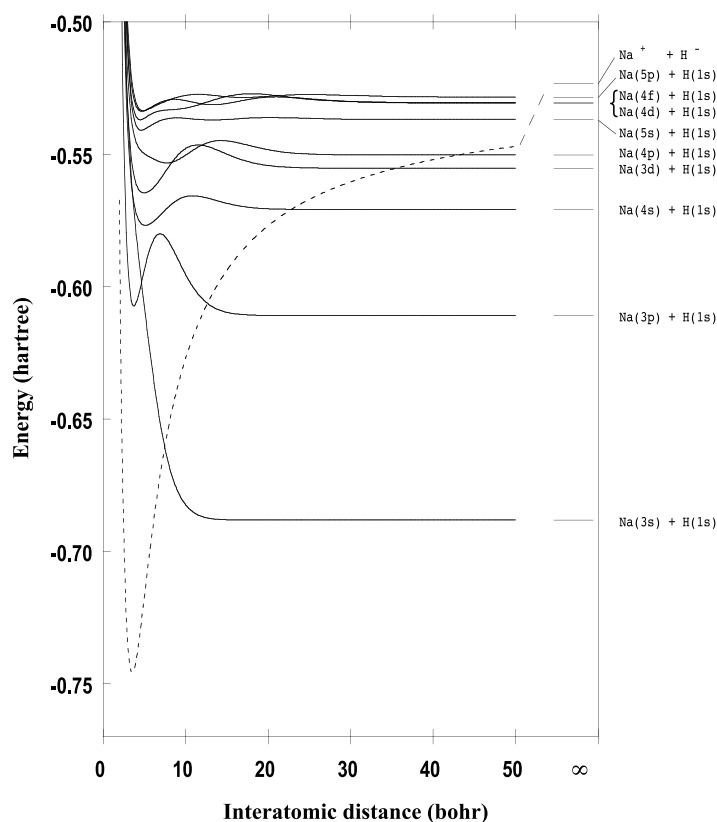


Figure 2. Diabatic energies for the lowest ten $^1\Sigma^+$ states of NaH: (—): states dissociating to neutrals; (---): ionic state.

Table 2. Main spectroscopic constants of NaH for the ground (X) and the first excited (A) states of $^1\Sigma^+$ symmetry. $\Delta E_{0,1}$ is the first vibrational spacing.

	X		A	
	Theory	Experiment ^a	Theory	Experiment ^a
D_e (cm^{-1})	15 787	$15\,900 \pm 100$	10 024	10 143
R_e (a_0)	3.568	3.566	6.057	6.035
$\Delta E_{0,1}$ (cm^{-1})	1117.4	1133.1	322.1	323.6

^a Stwalley (1991).

From table 2 it can be seen that the main spectroscopic constants for the X and A states are in satisfactory agreement with experiment (Stwalley 1991). No spectroscopic information is available on any of the other states (Stwalley 1991). The *ab initio* calculation thus leads to accurate results for the asymptotic (table 1) and also for the molecular equilibrium regions (table 2), essential requirements for a good estimate of the neutralization cross section.

As is readily seen in the diabatic picture (figure 2), the ionic curve crosses progressively all the neutral ones. Because the couplings between the neutral and the ionic wavefunctions are not constant across the crossing region, the positions of the minima in the potential splittings at the pseudocrossings do not coincide with those of the real crossings between the diabatic curves.

Table 3. Na(*nl*)H(1s) and Na⁺H[−] pseudocrossing properties.

(<i>nl</i>)	R _{<i>nl</i>} (a ₀)	Δ _{<i>nl</i>} (eV)	<i>v</i> _{<i>nl</i>} [*] (au)	<i>v</i> _{<i>nl</i>} th (au)
3s	7.53 ^a	1.23		
	7.60 ^b	1.21		
	7.65 ^c	1.17		
	7.85 ^d	1.13		
	7.83 ^g	1.20	0.187	0.0120
3p	13.08 ^a	0.427		
	13.28 ^b	0.407		
	13.67 ^d	0.423		
	12.6 ^e	0.421		
	13.61 ^g	0.394	0.061	0.0091
4s	21.96 ^a	0.069		
	22.8 ^e	0.043 5		
	22.4 ^f	0.16		
	23.5 ^g	0.046 0	0.002 5	0.0070
4s ^h	5.12 ^g	0.043		
3d	35.4 ^e	0.003 35		
	34.0 ^f	0.049		
	35.9 ^g	0.006 86	0.000 13	0.0056
4p	43.0 ^e	0.001 04		
	40.0 ^f	0.022		
	43.2 ^g	0.001 85	0.000 014	0.0051

^a Olson and Kimura (1985).^b Olson and Liu (1980).^c Stwalley (1991).^d Belyaev *et al* (1999).^e Janev and Radulovic (1978).^f Fleck *et al* (1991), estimated from results of Bruna and Pyrimhoff (1987).^g This work.^h Inner crossing—see text.

The pseudocrossing positions and splittings are compared with previous estimates in table 3. Our values have been obtained from a least-squares fit to the Landau–Zener form of the adiabatic interaction in the pseudocrossing region and the precise values obtained depend slightly on the choice of *ab initio* points employed in the fit. Our positions are systematically at larger distances than in the previous calculations, apart from a very slightly larger value for the X–A and 2–3 pseudocrossing distances obtained by Belyaev *et al* (1999). It is well known that an accurate estimate of the H electron affinity requires a huge Gaussian basis set, including high angular momentum functions, in order to account for the angular correlation energy. None of the basis sets used for the previous NaH calculations was large enough, leading to an underestimate of the H electron affinity and hence of the crossing distances. Taking advantage of the diabatic approach, our results have been corrected for this underestimate and when the ionic curve is lowered the crossings shift to larger distances. The shift is particularly important for the long-range crossings where the ionic curve flattens as $\frac{1}{R}$ and a small decrease in the asymptotic energy splitting may lead to a large shift.

For the X–A pseudocrossing all the separations, apart from that of Belyaev *et al* (1999), are within 3% of our value. For the 2–3 pseudocrossing our splitting is the smallest, with other values up to 8% greater. Differences between the various calculations at the remaining crossings are much greater, exceeding a factor of two in some cases.

3. Cross sections

3.1. Mutual neutralization

At these energies a fully quantal treatment of the relative motion is required. The procedure is similar to that described in our earlier paper (Croft *et al* 1999a). While our primary interest is in the low-energy regime now accessible in merged-beam experiments, to compare with the results of Olson and Kimura (1985) we have determined the cross section up to their lowest energy, 96.6 eV (100 eV u^{-1}). A ten-state calculation has been employed, including the states discussed above. In the very low energy region, $E \lesssim 1 \text{ eV}$, ≈ 450 partial waves are required for convergence, increasing to ≈ 2500 at 100 eV.

To aid a qualitative understanding of the results we introduce the Landau–Zener critical velocity, v_{nl}^* for the nl transition where (Child 1979)

$$v_{nl}^* = (\pi/2) \Delta(nl)^2 R_c^2 \quad (5)$$

and we have assumed one Coulomb and one negligible interaction in determining the difference in the slope at the pseudocrossing point. For $v \ll v_{nl}^*$ the crossing is traversed adiabatically and the transition probability at the nl crossing is exponentially small, varying as $\exp(-v_{nl}^*/v)$, where v is the speed at the crossing point. For $v \gg v_{nl}^*$ the crossing is essentially diabatic and the probability of an adiabatic transition after both passages through the crossing point is proportional to v_{nl}^*/v . In a two-state model the cross section peaks at $v = 2.35 v_{nl}^*$ (Child 1979). Values for v_{nl}^* are included in table 3. For convenience we have also included the speed at threshold at the nl crossing point, v_{nl}^{th} .

We recall that Errea *et al* (1986) have shown that the Landau–Zener parametrization of the non-adiabatic coupling at the crossing points is poor for the 3s and 3p couplings but is more satisfactory for the outer crossings. Since these are our primary interest, a Landau–Zener analysis should assist a qualitative understanding of our coupled-channel results.

Total cross sections, σ_{Tot} , for collision energies between 0.01 and 100 eV are shown in figure 3. Also shown are the partial cross sections, σ_{nl} , to the most populated final states: $\text{H}(1s) + \text{Na}(nl)$, with $nl = 3p, 4s, 3d$ and $4p$. Results are compared with values obtained from the figure of Janev and Radulović (1978). Table 4 contains our results for all final states.

In the very low energy regime, below $\approx 1 \text{ eV}$, the cross sections vary inversely with energy, as obtained previously in coupled-channel calculations for H^+/H^- (Fussen and Kubach 1986) and Li^+/H^- (Croft *et al* 1999b). Such behaviour arises from the focusing effect of the Coulomb field (see, e.g., Croft *et al* 1999b). Our results for σ_{Tot} are $\approx 15\%$ larger than those obtained by Janev and Radulović (1978), a comparable difference to that obtained earlier for Li^+/H^- (Croft *et al* 1999a).

Approximately 85% of σ_{Tot} in this low-energy region comes from σ_{4s} , with a slightly smaller ratio obtained by Janev and Radulović (1978). The cross section for 4s production is boosted by an inner avoided crossing between the $3-4 \text{ } ^1\Sigma^+$ states at $R \approx 5 a_0$ (see figure 1) with a minimum separation of 43 meV, fortuitously quite close to the value obtained for the outer crossing between these states, see table 3, and the speed at this crossing point is close to that at the outer crossing point. As noted above, the parameters for the outer crossing obtained by Janev and Radulović (1978) are very similar to those calculated here. At threshold we have $v_{4s}^{\text{th}} = 0.0070 = 2.8 v_{4s}^*$ so the transition probability is high and this cross section is near its maximum and hence insensitive to the precise splitting.

The next most important partial cross section for this low-energy region is, in our calculation, σ_{3d} . For this at threshold we have $v_{3d}^{\text{th}} = 44 v_{3d}^*$. Our splitting for this transition at the avoided crossing is approximately twice that obtained by Janev and Radulović (1978), qualitatively consistent with our cross section being a factor of 2.4 times larger. For the even

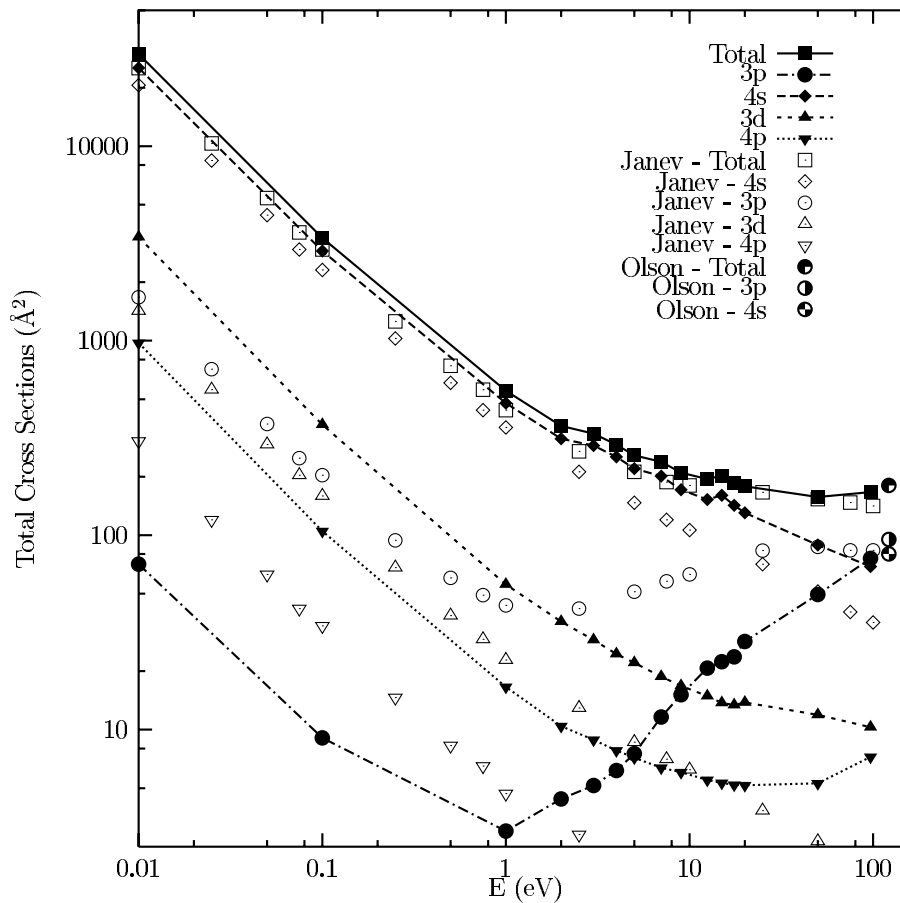


Figure 3. Cross sections for $\text{Na}^+ + \text{H}^- \rightarrow \text{Na}(nl) + \text{H}(1s)$. Results shown as Janev are from Janev and Radulović (1978), those shown as Olson are from Olson and Kimura (1985). For clarity their 100 eV u^{-1} results are plotted at 125 eV .

more distant ($R_C = 43 a_0$) $4p$ crossing where $v_{4p}^{\text{th}} = 0.0051 = 376 v_{4p}^*$ our calculated cross section is about three times that of Janev and Radulović (1978), consistent with the differences in the couplings shown in table 3.

The most striking difference arises for the $3p$ cross section where our value is about 20 times smaller than that of Janev and Radulović (1978). For this transition at threshold $v = 0.15 v_{3p}^*$, with either set of coupling parameters. While the inner $3-4 \ ^1\Sigma^+$ avoided crossing will lead to a loss of flux to $\text{Na}(3p)$ not included in the description of Janev and Radulović (1978), such a large effect is surprising.

For higher energies, $E \gtrsim 1 \text{ eV}$, trajectory effects become much less important. For those crossings where $v \gg v^*(4s, 3d, 4p)$ the cross section falls off approximately as $1/v$, with the relative positions of our values and those of Janev and Radulović (1978) similar to those found at low energies. For the $3p$ transition we have $v < v_{3p}^*$ for the energies of interest so the cross section is increasing as v increases and the transition becomes less adiabatic. The cross section for production of $3s$ is small and will be discussed below in the context of the inverse process: ion-pair production.

Table 4. Cross sections, in \AA^2 , for $\text{Na}^+ + \text{H}^- \rightarrow \text{Na}(nl) + \text{H}(1s)$.

E (eV)	nl								
	3s	3p	4s	3d	4p	5s	4d	4f	5p
0.01	0.094	70.9	25 300	3410	974	1.28	0.054	0.36	0.26
0.10	0.004	9.07	2 890	370	105	0.38	0.12	0.32	0.30
1.0	0.004	3.0	477	55.8	16.6	0.10	0.088	0.028	0.13
2.0	0.003	4.4	313	36.0	10.4	0.11	0.080	0.0070	0.12
3.0	0.002	5.2	289	28.9	8.87	0.11	0.029	0.0316	0.10
4.0	0.004	6.2	252	24.5	7.80	0.12	0.072	0.0072	0.15
5.0	0.009	7.5	220	22.0	7.17	0.11	0.15	0.042	0.045
7.0	0.012	11.6	201	18.7	6.37	0.14	0.068	0.077	0.089
9.0	0.014	15.1	171	16.8	6.03	0.16	0.033	0.093	0.30
12.5	0.018	20.7	153	14.9	5.52	0.11	0.13	0.064	0.21
15.0	0.032	22.4	160	13.7	5.32	0.053	0.24	0.12	0.18
17.5	0.043	23.7	142	13.4	5.20	0.166	0.29	0.13	0.18
20.0	0.066	28.4	130	13.8	5.17	0.129	0.28	0.14	0.10
50.0	0.63	49.4	89	11.9	5.29	0.199	0.30	0.15	0.23
96.6	1.90	76.0	69	10.3	7.24	0.201	1.02	0.38	0.71

At $E = 100 \text{ eV u}^{-1}$ the values of Olson and Kimura (1985) are about 6% larger than ours for σ_{Tot} , about 25% larger for σ_{3p} and σ_{4s} and about 20% smaller than ours for σ_{3s} and hence very much smaller than the value of Janev and Radulović (1978) for this cross section. The closer agreement for σ_{Tot} than for the partial cross sections may partly be due to the different bases employed in the two calculations: ten $^1\Sigma^+$ states in our case and six $^1\Sigma^+$ and two $^1\Pi$ states by Olson and Kimura. Given the differences in the potentials and couplings employed and the uncertainties in reading their values from their figure, the agreement with these results is quite satisfactory.

3.1.1. Low-temperature rate coefficient. We have used our low-energy results to estimate the total rate coefficient, k , for mutual neutralization. We find $k(T) = 3.0 \times 10^{-7} (T/300 \text{ K})^{-1/2} \text{ cm}^3 \text{ s}^{-1}$, useful for temperatures up to $\approx 10\,000 \text{ K}$. From their figure we estimate that Janev and Radulović (1978) obtain $k(T) = 2.7 \times 10^{-7} (T/300 \text{ K})^{-1/2} \text{ cm}^3 \text{ s}^{-1}$. In their review of rate coefficients for astrophysical applications Millar *et al* (1997) list $k(T) = 2.3 \times 10^{-7} (T/300 \text{ K})^{-1/2} \text{ cm}^3 \text{ s}^{-1}$.

3.2. Ion-pair production

Here we discuss the cross section for ion-pair production, σ_{nl}^{IP} , from $\text{Na}(nl) + \text{H}(1s)$ collisions. These cross sections may be determined from the mutual neutralization cross sections by detailed balance, however it is more convenient to discuss them separately. Results are compared in figure 4 with those of Janev and Radulović (1978) and of Olson and Kimura (1985). Measurements of this process are available (Nagata 1980, Howald *et al* 1984) but only for energies above 650 eV. It can be seen that at 100 eV our 3s cross section is in good agreement with that of Olson and Kimura (1985). The better agreement apparent here than for the mutual neutralization cross section to this state simply reflects uncertainties in reading their values. For σ_{3s} our values are between one and three orders of magnitude smaller than those calculated by Janev and Radulović (1978). This difference is not dissimilar to that observed above for transitions involving the 3p level.

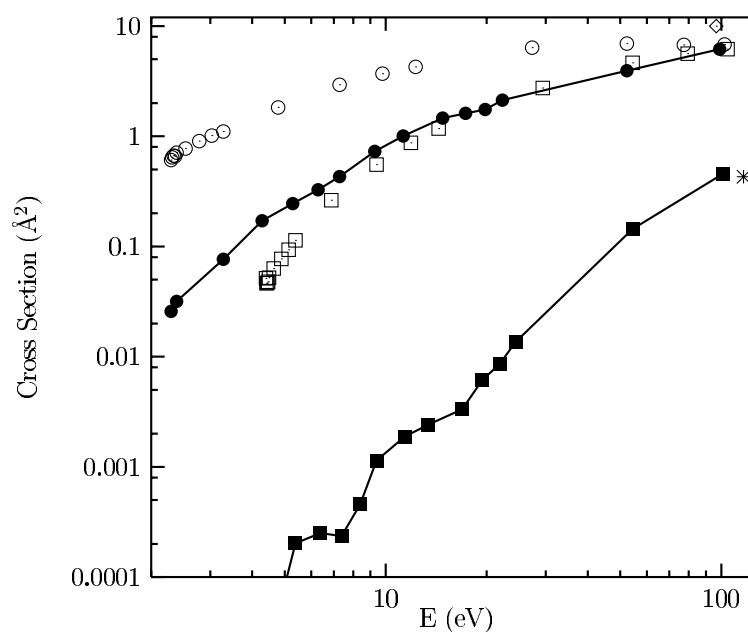


Figure 4. Ion-pair production cross sections in Na(3l) + H(1s) collisions. From 3s: (■), this work; (□), Janev and Radulović (1978); (*), Olson and Kimura (1985). From 3p: (●), this work; (○), Janev and Radulović (1978); (◇), Olson and Kimura (1985). The 3s result of Olson and Kimura (1985) at 100 eV u⁻¹ has been displaced to 110 eV for clarity.

We have estimated the cross section from the 3p level assuming that rotational coupling, which is not included in our calculations, would not make a significant difference. Our value is about 35% smaller than that of Olson and Kimura (1985) and, at 100 eV, 10% below that of Janev and Radulović (1978). As noted above, at lower energies the differences with that calculation are much larger.

4. Summary and conclusions

Using a ten-state molecular expansion we have calculated cross sections for mutual neutralization in Na⁺ + H⁻ collisions for energies between 0.01 and 100 eV. A quantal description of the relative motion has been employed, combined with *ab initio* diabatic potentials and couplings. The total neutralization cross sections are ≈15% larger than those obtained by Janev and Radulović (1978). At 100 eV our values are about 6% smaller than those of Olson and Kimura (1985). Consistent with the calculations of Janev and Radulović (1978) we find that, below about 10 eV, ≈85% of the neutralization cross section leads to Na(4s). For the remaining neutralization channels the differences can be much larger. The low-temperature rate coefficient for mutual neutralization has been estimated.

We have also used our results to evaluate the ion-pair production cross section in Na(3l) + H(1s) collisions. For both the 3s and the 3p initial levels the cross section rises rapidly with increasing energy. At 100 eV our results for 3s and 3p are within 5% and 35%, respectively, of those obtained by Olson and Kimura (1985). Part of the larger discrepancy for the 3p level may arise from our neglect of rotational coupling so that no contribution is obtained from the 3p_{|m|=1} entrance states.

A comparison with measurements of mutual neutralization, particularly if final-state selection could be achieved, or of low-energy ion-pair production cross sections, would allow discrimination between the various theoretical results for this process.

Acknowledgments

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