Theoretical study of Na(3p) excitation in Na-Ne collisions

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Abstract. Na(3p) excitation in Na-Ne collisions is analysed in terms of two independent mechanisms: (i) at low energy via two curve crossings leading to the simultaneous excitation of Ne atoms; (ii) at high energy by a direct transition. Diabatic potential energy curves and couplings are calculated using *ab initio* methods. The scattering equations are solved (quantally for mechanism (i) and by the impact-parameter method for mechanism (ii)). Total cross sections are calculated and agree reasonably well with the experimental results. In particular, the threshold behaviour is well reproduced by a seven-state model and at high energy the agreement between theory and experiment is improved with respect to previous work.

1. Introduction

Alkali-atom-rare-gas-atom collisions and alkali-earth-ion-rare-gas-atom collisions form a class of colliding systems characterised by the presence of an 'isolated' electron outside two closed-shell cores and are therefore often referred to as 'quasi-one-electron' systems. Experimental work was mainly devoted to the measurement of total cross sections for excitation of the resonance line (np - ns) of the alkali atom or the alkali earth ion (Olsen *et al* 1977, Mecklenbrauck *et al* 1977). Generally these cross sections display two distinct regions as a function of energy: rising from threshold to a first flat maximum at energies of a few hundred to a few thousand eV (low energy part), the cross section then presents a second neat maximum at a much higher energy. The high energy part is usually ascribed to a direct $3s \rightarrow 3p$ transition undergone by the 'active' electron. Nielsen and co-workers have calculated the total cross sections for Be^+ and Mg^+ excitation in collision with rare gases (Nielsen and Dahler 1976) and Li, Na in collision with rare gases (Manique *et al* 1977). All these calculations are based on a 'one-electron' effective potential description of the quasi-molecule. Although the general trends of the experimental cross sections are qualitatively well reproduced by their calculations, quantitative agreement is only obtained with light collision partners (Li-He, Be^+ -He) and especially with He targets. The disagreement for heavier systems was attributed to the inaccuracy of the effective potentials. This was confirmed for the Na-Ne case of interest here, as shown recently by Masnou-Seeuws *et al* (1978).

The threshold region and the low energy part of the total cross sections for the alkali-resonance line were investigated by Kempter *et al* (1974). These authors proposed that the excitation transition was induced at low energy via a curve crossing, following the suggestion of Anderson *et al* (1969). Later, Fayeton *et al* (1976)

measured characteristic energy losses and differential cross sections for the alkali-earth-ions-rare-gas collisions. Basing their analysis on the electron promotion model, these authors suggested that the alkali-ion excitation should actually be induced *indirectly* by two successive curve crossings via the core-core interaction. With this model they could explain the strong simultaneous excitation of the rare-gas partner in $\text{Mg}^+ - \text{Ne}$ using quasi-symmetry arguments.

However, to our knowledge, no quantitative calculations were performed for such a mechanism. In this paper we present a theoretical treatment of both types of mechanisms, i.e. direct excitation and excitation through core interaction for the $\text{Na} - \text{Ne}$ collision using '*ab initio*' potentials. A preliminary account of this work has recently been published (Pedersen *et al* 1978) together with proof of the existence of both mechanisms based on a coincidence experiment performed in Aarhus.

2. Quasi-molecular background—qualitative analysis

The interaction between two closed L-shell systems is now well understood. In particular, Gauyacq (1978a, b) performed extensive calculations on the Ne_2 system which is isoelectronic with $\text{Na} - \text{Ne}^+$. This investigation essentially confirms the MO correlation diagram proposed by Lichten (1967). Tolk *et al* (1976) extrapolated this correlation diagram to $\text{Na}^+ - \text{Ne}$. The recent '*ab initio*' treatments of this system (Olsen *et al* 1979) provide a more accurate correlation diagram that can well describe the core of the $\text{Na} - \text{Ne}$ system. The additional $3s_{\text{Na}}$ electron is initially in the 'unpromoted' $3s\sigma$ valence MO. From the diabatic MO correlation rules no crossing of this orbital with Rydberg orbitals is expected. These considerations lead to the diabatic $\text{Na} - \text{Ne}$ MO correlation diagram shown in figure 1. What can we learn from such a diagram?

Figure 1. MO correlation diagram of $\text{Na} - \text{Ne}$ estimated from the SCF calculation of the $(\text{NaNe})^+ {}^1\Sigma^+$ state. $\circ$, quasi u-g crossing; $\otimes$, quasi u-u crossing; $\square$, strong rotational coupling; ①, mechanism (i); ②, mechanism (ii).

2.1. Mechanism (i)

At low energy, provided the collision is violent enough for the Na-Ne⁺ core interaction to be effective, the promoted $4f\sigma$ orbital offers an alternative for $3s \rightarrow 3p$ excitation through the 'bridged' C-C' crossings. However, in this case, the 'diabaticity' of the C crossing will be crucial. If the C crossing is very adiabatic, the $3s\sigma$ electron will be transferred to the $4f\sigma$ orbital and will subsequently suffer transitions leading to Na($3p$) excitation. On the other hand if the C crossing is very diabatic, the $2p_{\text{Ne}}$ electrons become active and may undergo transitions at the C' crossing leading in turn to single and double Ne excitations. Actually an important transition probability at the C crossing has been observed (Mecklenbrauck *et al* 1977).

More can be learnt from the many-electron state correlation diagram in which the molecular states are constructed as single configurations of the MO of figure 1. For the sake of clarity only the first σ and π Rydberg orbitals are introduced in the scheme in addition to the $4f\sigma$ and $3s\sigma$ MO describing the incident channel. Even with this limited number of MO, 7Σ states, 5Π states and 2Δ states are constructed leading to the pattern shown in figure 2. These states are distributed in various series according to the number (0, 1, 2) of electrons in the promoted $4f\sigma$ MO. Obviously this scheme only deals with transitions occurring at short internuclear distance and can by no means represent the 'intra-series' interaction responsible for the population sharing between the various excited channels in each series. This problem of the correct atomic dissociation of the

Figure 2. Schematic simple configuration state correlation diagram of Na-Ne for zero-, one- and two-electron excitation in the lowest $3s\sigma$, $4p\sigma$ and $3p\pi$ orbitals shown in the insert. The γ (γ') ($\odot$) crossings reflect the C (C' MO) crossings. The interaction at crossings of the same type (γ or γ') is approximately the same $H_\gamma \approx H_{C'} = \langle 4f\sigma | H_{el} | 3s\sigma \rangle$ and $H_{\gamma'} \approx H_{C'} = \langle 4f\sigma | H_{el} | 4p\sigma \rangle$. The full circles correspond to crossings between states differing by two molecular spin orbitals (MSO) and coupled only by electron correlation.

quasi-molecular state is outside the scope of this paper. Due to the steep promotion of the $4f\sigma$ MO, all the γ , γ' state crossings reflecting respectively the C and C' MO crossings, are located over a small range of internuclear distances. If this region is reached, one- and two-electron transitions towards the initially empty ($4p\sigma$) or partially filled ($3s\sigma$) MO would feed the A and C series giving rise to the triple peak behaviour of the energy-loss spectra (see e.g. Kessel and Fastrup 1973). This feature is commonly observed both in inner-shell and outer-shell excitation processes (see e.g. Brenot *et al* 1975a, b). Provisionally ignoring the secondary transitions to the B series, the triple peak should be seen as strong peaks corresponding to the $\text{Na} + \text{Ne}^*$ and $\text{Na} + \text{Ne}^{**}$ channels. This is just what we have observed in our laboratory (figure 3). Exotic channels like $\text{Na}^{-(*)} + \text{Ne}^+$ and $\text{Na}^+ + \text{Ne}^{-*}$ can also, in principle, be excited. But at present no experimental work has been devoted to the search for such states.

Figure 3. (a) Typical energy-loss spectrum, obtained by a time of flight technique, of scattered Na atoms from the Na-Ne collisions at 1 keV and 8.4° scattering angle. The three peaks correspond to zero-, one- and two-electron excitation of the Ne atom. The $\text{Na}^*(3p)$ excitation is not resolved. (b) Relative differential cross section (DCS) at 2 keV, for the above A, B and C processes. Also shown is the $\text{Na}(3p)$ DCS from the coincidence experiment of Pedersen *et al*.

Let us now consider the effect of the secondary A-B and C-AB crossings. The interaction at these crossings will lead to a sharing of the population of the A states among $\text{Ne} + \text{Na}^*$ channels ($A \rightarrow B$) and that of the C states among $\text{Ne}^* + \text{Na}^*$ ($C \rightarrow AB$). The other possible schemes of population sharing as $C \rightarrow B$ should not be very important, since they involve 'direct' two-electron transitions (electron correlation) which are generally much weaker than one-electron transitions. On the other hand it

has been demonstrated by Gauyacq (1978a, b) that in Ne–Ne collisions simultaneous excitation of both Ne atoms in a two-step process ($X \rightarrow A_2 \rightarrow C_2$) is responsible for about 30–50% of the total Ne excitation cross section. A similar ratio is expected here since the primary mechanism is the same. After the population sharing from the A_2 (C_2) states at the γ_2 (γ_3) crossing, a similar 30–50% population is expected to come from the $Na^* + Ne^*$ channel, a possibility which was disregarded in a previous qualitative interpretation (Mecklenbrauck *et al* 1977).

Up to now, we have dealt only with Σ states. Actually the scheme is further complicated by the introduction of Π states. A large $4p\sigma \rightarrow 3p\pi$ population sharing (figure 1) by rotational coupling is known to be responsible for the dominant 3p excitation in symmetric and quasi-symmetric collisions (Gauyacq 1978a). This effect will appear here as a population transfer from the $A^2\Sigma$, $C^2\Sigma$ states to their associated Π states (figure 2). Although this population transfer should not drastically change the total cross section for Na(3p) excitation, its role will obviously be crucial in the polarisation analysis of the emitted light.

2.2. Mechanism (ii)

Direct $3s_{Na} \rightarrow 3p_{Na}$ transitions are not favoured at low energy due to the lack of $3s\sigma - 4p\sigma$ MO crossings. As discussed by Olsen *et al* (1977), the energy range for which the direct transition occurs can be estimated from the ‘Massey criterion’. The use of an energy difference between the atomic levels $\Delta E = 2.1$ eV, and an effective range $\Delta R \approx 5$ au leads to a value $E_{lab} = 9$ keV, which is in good agreement with the energy corresponding to the maximum of the experimental cross sections ($E_{lab} = 15$ keV).

3. Molecular calculation—cross sections

For both types of mechanism, use of a diabatic representation leads to more simple calculations since this procedure does not require the calculation of $\langle |d/dR| \rangle$ matrix elements. The frozen-orbital approximation (Gauyacq 1978a, b) is a simple method used to obtain such a diabatic representation in the vicinity of MO crossings. Actually this method consists of freezing the electronic clouds around the nuclei at a characteristic internuclear distance R_F close to the interaction region characteristic of each mechanism; the orbital set calculated at R_F is kept for all internuclear distances $R < R_F$. Mechanism (i) occurs at very small internuclear distances where the incident state has already acquired a strong molecular character: $R_F = 2$ au has been chosen as explained below. Mechanism (ii) occurs at a much larger distance where the atomic character is mainly conserved. In this case we have then frozen the atomic orbitals (in practice $R_F = 20$ au).

3.1. Short-range mechanism (i)

3.1.1. Potential and coupling calculations. The calculations start from LCAO–STO–MO expansions (linear combination of atomic Slater-type orbital–molecular orbital). The STO expansion basis is the same as that found in the Ne_2 system used by Gauyacq (1978a). It has been checked that the Ne_2 basis can correctly describe the Na atom in its ground and first excited states. The calculated Na 3s–Na 3p energy separation amounts to 2.05 eV which is very near the experimental value of 2.1 eV. An SCF calculation has

been carried out on the $(\text{NaNe})^+ \times {}^1\Sigma^+$ ground state using the *ALCHEMY* program of Bagus *et al* (1971). This choice should correctly describe the incident channel, the first excited channel $\text{Ne} + \text{Na}^*(3p)$, and the transitions at the $4f\sigma$ - $nl\sigma$ MO crossings. The outer MO ($4f\sigma$ and Rydberg MO) are frozen at $R_F = 2$ au, where the $4f\sigma$ promotion becomes significant (figure 1). On the other hand, the inner MO are not frozen in order to describe the core relaxation well. The single-configuration excited states which should play a significant role in the collision process were selected according to qualitative interpretation (of § 1). These states were obtained in the virtual orbital method (Roothaan 1951) and describe the

B series	$(\dots)(4f\sigma)^2(nl\sigma)_{\text{Ryd}}$
A series	$(\dots)(4f\sigma)(3s\sigma)(nl\sigma)_{\text{Ryd}}$
AB series	$(\dots)(4f\sigma)(4p\sigma)(n'l'\sigma)_{\text{Ryd}}$
C series	$(\dots)(-)^{\circ}(3s\sigma)(nl\sigma)(n'l'\sigma)_{\text{Ryd}}$.

As expected from the qualitative model, the A, AB and C series cross both the incident channel and the B series (figure 4). This multi-crossing pattern occurs for $1.2 < R < 1.7 a_0$.

Figure 4. Potential energies of the Na-Ne system, in the X, A, B, AB crossing region. Energies are referred to that of $\text{Na}(3s) + \text{Ne}(2p^6)$ at $R = \infty$. —, Σ states; — —, Π states.

Inclusion of all states of the A, AB and C series in the scattering coupled equation would result in an enormous and prohibitively expensive calculation. A careful selection of the most important states thus requires examination of the coupling terms.

However the single-configuration representation and frozen-orbital procedure introduces strong intra-A, intra-AB and intra-C series couplings which mixed all these states preventing such direct selections. The more significant states, at least in the crossing regions, are obtained by a limited configuration interaction (LCI) in the subspace spanned by the 14 lowest Σ states and 14 Π states of the A + AB series as well as the 14 lowest Σ states and 18 Π states of the C series. This procedure enables us to preserve the diabatic character of the relevant crossings. We are thus allowed to select the A + AB and C states having the strongest interactions with the X and B states in the velocity range of interest. This method is designed to prevent strong rapid mixings between the basic configurations that correspond to zero-, one- and two-electron excitation from the $4f\sigma$ MO as suggested by qualitative analysis. Let us examine first the case of simultaneous excitation of Ne^* and Na^* (AB series). These channels can be either directly populated through a $2e^-$ (electron correlation) X-AB transition or by the more indirect, but maybe more efficient (one-electron transition) X-A-C-AB successive crossings. The inclusion of these mechanisms would require at least twelve significant states; a set which is still too lengthy to be handled. We have therefore only included the X, A + AB, B series, neglecting the excitation of two $4f\sigma$ electrons. This does not mean that the deleted mechanism is unimportant; it is even thought to be dominant in the 1–4 keV laboratory energy range. However in the threshold region ($E_{\text{lab}} < 0.4$ keV) single $4f\sigma$ electron transitions strongly dominate as shown for the Ne-Ne system (Gauyacq 1978a, b). Justifying deletion of doubly excited states for $E_{\text{lab}} < 400$ eV, the most important states of the A series will be those which have large electronic interactions with both the X and B states. Actually four A states have a much larger interaction than the other A states. These interactions are typically in the range $H_{XA_n} = 0.02\text{--}0.09$ au, $H_{B_1A_n} \approx 0.03\text{--}0.08$ au at $R = 1.6 a_0$; all these crossings correspond to quasi u-u interactions and, as expected, have a much larger interaction than the first quasi u-g crossing ($H_{XA_1} \approx 0.007$ au). However we have included this state in the collision treatment to study its influence at the very threshold. The calculated curves in the crossing region are given in figure 4.

From the study of Ne-Ne collisions by Gauyacq, we have learned that in L-shell-L-shell interactions the Π states of the A series are negligibly coupled to the incident $x^2\Sigma^+$ state. However, a large population of these Π states from the Σ states of the A series is induced by a strong rotational coupling ($4p\sigma \rightarrow 3p\pi$). For the present system, this mechanism will result in a $\pi 3p_{\text{Na}}$ channel ($B^2\Pi$ state) population at short internuclear distances via the $x^2\Sigma^+ \rightarrow A^2\Sigma^+ \rightarrow A^2\Pi \rightarrow B^2\Pi$ successive transitions. Actually, this process is just a population transfer between Σ and Π states of the A series which should not strongly affect the total cross section. In order to check this assumption we have performed two sets of calculations: (i) with only Σ states; (ii) with both Σ and Π states.

3.1.2. Scattering calculations. The quantum close-coupling equations for the scattering problem were solved using the Gordon method (Gordon 1969, 1971) modified by Stern *et al* (1978) at centre of mass energies $E_{\text{CM}} = 60, 70, 80, 90, 100, 150, 200$ and 300 eV. The transition probabilities have been obtained for partial wavenumbers spaced by $\Delta l = 5$ at $60\text{--}70$ eV, $\Delta l = 10$ at $80\text{--}150$ eV and $\Delta l = 20$ at $E_{\text{CM}} = 200\text{--}300$ eV. The S matrix converged at $R = 20 a_0$ to an accuracy of 10^{-3} .

Consider now transition probabilities. In order to understand the relative importance of the various states of the A series better, we performed four and seven coupled-state calculations. For the four-state calculations, only the first (quasi g) A_1 state and the first (quasi u) A_2 state are added to the $x^2\Sigma^+$ and $B^2\Sigma^+$ state. The three

Figure 5. Transition probabilities for mechanism (i) versus the partial-wave number. 1 incident channel, 2 Na(3p) channel, 3...7 various intermediate states, of the A and AB series. It should be noted that state '3' corresponds to A_1 state; mainly described by the $(4f\sigma)(3s\sigma)^2$ simple configuration state, and similarly state '4' primarily corresponds to the $(4f\sigma)(3s\sigma)(4p\sigma)$. The inserts show the most populated states at various threshold energies.

other most significant A_n states have been included in the seven-state calculations. Figure 5 shows the transition probabilities versus partial wavenumber (or equivalently impact parameter $b = l/k$). At 60 eV, excitation of Na(3p) is, by far, dominant. At higher energy the Ne^* population increases and becomes even larger than the Na^* population illustrating the increasing 'diabaticity' of the A-B crossings with energy. Furthermore it is readily seen that inclusion of the extra $3A_n$ states in the seven-state calculation (figure 5(c)) substantially increases the Na(3p) transition probability. This demonstrates that several A_n states actively participate in the $\text{Na}^*(3p)$ population. One can also notice that the Na(3p) excitation probability ('1→2' in figure 5) becomes important (≥ 0.1) at the same energy $E_{\text{CM}} = 70$ eV where the Ne^* excitation probability is large. Finally the first quasi u-g crossing plays a role only at threshold since the A_1 state is more populated than the other A_n states only at 60 eV. It is noteworthy that the Stueckelberg oscillations only show up at $E_{\text{CM}} \geq 90$ eV when the turning point can reach internuclear distances smaller than that of the innermost crossing (figure 4). In the preliminary account of this work, we have shown that the theoretical $\text{Na}^*(3p)$ excitation probability is in agreement with the experimental impact-parameter dependence (Pedersen *et al* 1978).

Figure 6. Total Na(3p) cross section. Experiment: ●●●, Mecklenbrauck *et al*; ◆◆◆, Olsen *et al*. Theory: (1) —, 7Σ states; — — —, 9Σ and Π states; (2) — — — —, including the effect of 'diexcited' channels.

The total Na*(3p) excitation cross section computed in the 7Σ model is shown (curve (1)) on figure 6. This cross section only refers to the excitation of the $B^2\Sigma$ state (Na*(3p) + Ne(2p⁶) channel) and does not include the contribution from the AB channels dissociating into Na*(3p) + Ne*(2p⁵nl) which of course contribute to the experimental cross section. Full calculations of the relative populations of all channels dissociating into (Na⁺(2p⁶) + Ne⁺(2p⁵))_{core} + 2e_{Ryd} would be too difficult. However a rough estimation of the importance of these channels relative to the Na*(3p) cross section can be done using the quasi u-g symmetry argument. As discussed by Tolk *et al* (1976) for the (Na⁺ + Ne⁺) + e_{Ryd} dissociation in Na⁺-Ne collisions one may consider that the Rydberg electron population feeds approximately half the Na⁺ and half the Ne⁺ core configuration. Extending this to both Rydberg electrons in the present case would result in considering that the contribution Q' of these channels to the Na*(3p) cross section is approximately $Q'(3p) = \frac{1}{2}q(3p, 3p) + \frac{1}{4}q(3s, 3p)$. $q(3p, 3p)$ ($q(3s, 3p)$) refers to the sum of all contributions where the two Rydberg electrons have the $\sigma 3p$ character (the $\sigma 3s$, $\sigma 3p$ characters). Adding this contribution yields the curve (2) in figure 6; contribution of the Na* + Ne* channels is seen to be negligible at the very threshold ($E_{CM} \leq 80$ eV). The experimental data of Mecklenbrauck *et al* (1977) concerns the line $3^2P_{3/2} - 3^2S_{1/2}$; weighting this cross section by the $Q_{3/2}/Q_{1/2}$ ratio measured by these authors, we obtain the experimental Na(3p) cross section also shown in figure 6.

Consider next the Ne* cross section and Q_{UV} cross section. Mecklenbrauck *et al* (1977) have also measured the total UV emission cross section. This UV emission corresponds both to direct excitation of Ne*(3s) and to cascade emission from Ne*(3p). In our calculations the sum of the cross sections Q_{Ne*} corresponding to all A and AB series refers to excitation of both Ne*(3s) and Ne*(3p) and cannot be compared directly to the experimental results since these calculated cross sections include the excitation of the metastable states of neon. Keeping this in mind, it is still worthwhile to compare the experimental Q_{UV} to the theoretical Q_{Ne*} (figure 7). The agreement is surprisingly very good, demonstrating at least that our model is reasonable.

Figure 7. Calculated total Ne* excitations cross section compared to the Q_{UV} emission measured by Mecklenbrauck *et al.* Experiment: ●●●●●; theory: —, 7 states; — —, 9 states.

It has been mentioned in § 2 (see figure 1) that a large $4p\sigma \rightarrow 3p\pi$ population transfer should occur at short internuclear distances. Inclusion of single configuration $(4f\sigma)(nl\sigma)(3p\pi)^2\Pi$ states (A_π series) and the $(4f\sigma)^2(3p\pi)$ $B^2\Pi$ state leads to the crossing scheme (figure 2) involving only one-electron transitions:

In addition to the six Σ states already considered we have included the $B^2\Pi$ state and the two states of the $A^2\Pi$ series which have, after the LCI procedure, the strongest rotational coupling with the selected $A_n^2\Sigma$ states. The nine coupled-state scattering equations have been solved for $40 \text{ eV} < E_{CM} < 200 \text{ eV}$. Total cross sections are plotted in figure 6 for $Q_{Na(3p)}$ and in figure 7 for Q_{Ne^*} . It is readily seen that the previous Σ state results are not strongly affected by inclusion of Π states.

3.2. Long-range mechanism (ii)

3.2.1. Potential and coupling calculation. A perturbed atomic basis is thought to be the most adequate way of explaining the direct excitation process, which has its maximum at high energy and occurs at large internuclear distance. The frozen atomic orbitals (FAO) are taken to be SCF orbitals at $R = 20 \text{ au}$ of the $(NaNe)^+ 1\Sigma^+$ state. Again this orbital set gives a correct description of the $3s_{Na}$ and $3p_{Na}$ orbitals (for the same arguments as discussed in § 3.1.1). The energies and couplings are calculated using single configuration states built from FAO of Na and Ne. The FAO are orthonormalised to each other by the Schmidt method in the following order: $1s_{Na}, 1s_{Ne}, 2s_{Na}, 2s_{Ne}, 2p_{0Na}, 2p_{0Ne}, 3s_{Na}, 3p_{0Na}, 3s_{Ne}, 3p_{0Ne}$ for the σ orbitals and $2p_{\pm 1 Na}, 2p_{\pm 1 Ne}, 3p_{\pm 1 Na}, 3p_{\pm 1 Ne}$ for the π orbitals. This procedure is an extension of the projected valence bond (PVB) method developed by Kubach and Sidis (1976) which has proved to be adequate for the treatment of the exchange processes occurring at large distance.

In a first approximation the study of $Na(3p)$ excitation, leaving the Ne atom as a spectator, involves the inner FAO of both atoms and the outer $3s, 3p_0, 3p_{\pm 1} Na$ FAO only, neglecting the other Rydberg states of Na. However to take into account the $3s_{Na}-3s_{Ne}, 3p_{Na}-3p_{Ne}$ exchange interaction, the equivalent outer $3s_{Ne}, 3p_{0Ne}, 3p_{\pm 1 Ne}$ FAO must be

included in the basis. The considered states are then constructed by placing the 'active' electron in one of these six lower excited FAO, the inner-shell configuration being left unchanged. The resulting states are $^2\Sigma^+3s_{\text{Na}}$, $^2\Sigma^+3p_{\text{Na}}$, $^2\Sigma^+3s_{\text{Ne}}$, $^2\Sigma^+3p_{\text{Ne}}$, $^2\Pi3p_{\text{Na}}$ and $^2\Pi3p_{\text{Ne}}$. The energy curves are calculated with the ALCHEMY program (Bagus *et al* 1971) for internuclear distances $1.5 \text{ au} < R < 20 \text{ au}$. The electronic coupling terms $\langle ^2\Sigma^+ | H_{\text{el}} | ^2\Sigma^+ \rangle$ and $\langle ^2\Pi | H_{\text{el}} | ^2\Pi \rangle$ are byproducts of these calculations. The present procedure does not yield fully diabatic states in the sense of Smith (1969) and some remaining $\langle d/dR \rangle$ couplings must be taken into account. However, it is expected that such $\langle d/dR \rangle$ couplings are small and therefore in a first step we have neglected them and have only considered the electronic coupling and the dominant $\langle ^2\Sigma^+3p_{\text{Na}} | L^- | ^2\Pi3p_{\text{Na}} \rangle$ rotational coupling (calculation Ca 1).

The validity of this 'diabatic' approximation needs to be tested by further examination of the effect of the neglected $\langle d/dR \rangle$ couplings. However, to take these couplings into account in the scattering problem requires the introduction of so called 'translational factors'. This problem has been discussed by Bates and McCarroll (1958), Schneiderman and Russek (1969) and recently by Thorson and Delos (1978). Neglecting the translational factors means that the dynamic coupling depends on the choice of the electron-coordinate origin. Since experimentally the dominant process is the direct $3s_{\text{Na}}-3p_{\text{Na}}$ excitation, it seems that the most consistent choice would be the Na centre. In such a calculation (Ca 2), the coupling terms involving Ne orbitals are of course questionable. However, these dynamical coupling terms which are involved in the population of Na(3p) levels via virtual transitions to Ne⁻ exotic states should not affect the cross section considerably (see § 3.2.2). As an alternative procedure, one can follow the suggestion of Taulbjerg and Briggs (1975). When the dynamic coupling matrix elements involve two orbitals of the same atom the coordinate origin of the electron is taken to be the nucleus of that atom. On the other hand if such elements involve orbitals of different atoms the coordinate origin of the electron is taken to be the centre of mass of the nuclei. This procedure was used in calculation Ca 3. In all cases, the relevant dynamic couplings $\langle ^2\Sigma^+ | d/dR | ^2\Sigma^+ \rangle$ and $\langle ^2\Sigma^+ | L^- | ^2\Pi \rangle$ have been evaluated using computer programs written by Sidis and Gauyacq. As expected, the calculated dynamic couplings depend on the choice of the coordinate centre. It is therefore important to evaluate their effect on the total cross section.

3.2.2. Scattering calculations and cross sections. The six-state coupled equations have been solved in the semiclassical impact-parameter approximation using the PAMPA program of Gaussorgues *et al* (1975). This method is known to be appropriate for high energy collisions and small scattering angles.

The coupled equations are solved for each impact parameter b in the interval $(-15 a_0, 15 a_0)$ of the abscissa along the incident direction. These limits are large enough to ensure that all coupling terms have vanished. To take the residual internuclear axis rotation into account, the final amplitudes for Σ_{3p} and Π_{3p} state are obtained from the equations

$$C_{\Sigma_{3p}}(\infty) = C_{\Sigma_{3p}}(z_0) \cos \alpha - C_{\Pi_{3p}}(z_0) \sin \alpha$$

$$C_{\Pi_{3p}}(\infty) = C_{\Pi_{3p}}(z_0) \sin \alpha + C_{\Sigma_{3p}}(z_0) \cos \alpha$$

where $z_0 = 15 a_0$ and $\alpha = b\langle L^- \rangle / \sqrt{2} R(z_0)$. As a straight-line trajectory is supposed, the internuclear axis at infinity corresponds to the incident direction. The transition probability P_{3p_0} and $P_{3p_{\pm 1}}$ are given by $P_{3p_0} = |C_{\Sigma_{3p}}(\infty)|^2$ and $P_{3p_{\pm 1}} = |C_{\Pi_{3p}}(\infty)|^2$. The

Figure 8. Transition probabilities for mechanism (ii) at various energies — — —, calculation Ca 1; — — —, calculation Ca 2. The insert shows the values of the radial and rotational coupling terms in the transition region. Radial coupling: — — —, $\langle 3s\sigma_{\text{Na}} | d/dR | 3p\sigma_{\text{Na}} \rangle$. Rotational coupling: — — — — —, $\langle 3p\sigma_{\text{Na}} | L^- | 3p\pi_{\text{Na}} \rangle$. — — — — —, $\langle 3s\sigma_{\text{Na}} | L^- | 3p\pi_{\text{Na}} \rangle$.

transition probabilities $P_{3p\text{Na}}$ are plotted versus the impact parameter b in figure 8 for several energies.

The comparison between the Ca 1 and Ca 2 results illustrates the effect of the dynamical coupling on the calculated transition probabilities. All curves slowly decrease with b , that is they are representative of non-localised transitions. It is readily seen that the probability maximises at $E_{\text{lab}} = 20$ keV. The probabilities $P_{3s\text{Ne}}$ and $P_{3p\text{Ne}}$ are smaller by more than one order of magnitude than $P_{3s\text{Na}}$ or $P_{3p\text{Na}}$. Although these probabilities are negligible compared to the $P_{3p\text{Na}}$, the omission of the Ne^- states from the calculations significantly alters the results (30%) (table 1). This can be understood since the correct description of the $3s\sigma$, $3p\sigma$ and $3p\pi$ MO requires the inclusion of $3s_{\text{Ne}}$, $3p_{\text{Ne}}$ atomic orbitals to give a good account of the exchange forces.

Table 1. Influence of the Ne^- states in the mechanism (ii): the $\text{Na}(3p)$ cross section in the three-state model ($^2\Sigma^+3s_{\text{Na}}$, $^2\Sigma^+3p_{\text{Na}}$ and $^2\Pi3p_{\text{Na}}$) and in the six-state model ($^2\Sigma^+3s_{\text{Ne}}$, $^2\Sigma^+3p_{\text{Ne}}$, $^2\Pi3p_{\text{Ne}}$ added to the preceding states).

E_{lab} (keV)	$\sigma_{\text{Na}(3p)}(\text{\AA}^2)$ three states	$\sigma_{\text{Na}(3p)}(\text{\AA}^2)$ six states
2.15	0.124	0.043
15	5.1	3.79
54	3.56	2.01

The typical couplings between the $3s_{\text{Na}}$ and $3p_{\text{Na}}$ states which are responsible for the direct transition are seen to be important for rather large distances $3 \text{ au} < R < 7 \text{ au}$ (figure 8).

Figure 9. Influence of the dynamic couplings on the total $\text{Na}^*(3p)$ excitation cross section. The present calculations: - - - - -, Ca 1 (neglecting the dynamic couplings); —, Ca 2 (the Na atom is chosen as the coordinate centre); — · — · —, Ca 3 (the centre of mass is chosen as the coordinate centre for certain couplings, see § 3.2.1).

The calculated $\text{Na}(3s-3p)$ (Ca 3) impact-parameter dependence was already shown to be in semi-quantitative agreement with experiment (Pedersen *et al* 1978). In figure 9, we compare the total cross section for the $\text{Na}(3s \rightarrow 3p)$ transition using the three approximations Ca 1, Ca 2 and Ca 3. It is readily seen that in all cases, the shape, the threshold and the position of the maximum are only very slightly changed. On the other hand the cross section value at maximum varies by $\pm 15\%$. As argued above, we think that the calculation Ca 2 is the most consistent procedure, and in figure 10, we compare the Ca 2 results with experimental data of Olsen *et al* (1977) and previous calculations (Manique *et al* 1977, Gross *et al* 1978). The calculations of Gross *et al* (1978) are more than one order of magnitude larger than the experimental cross section. Manique *et al* (1977) reports an even larger cross section. Furthermore, an important shift of the maximum of the cross section is seen in both calculations. Although the present results improve the agreement with experiment, they are still too large by a factor of about three, which is unlikely to be explained by the effect of neglecting the translational factors as shown above. One obvious source of the overestimation of the $3s \rightarrow 3p$ excitation cross section comes from the neglect of the inner crossing processes (mechanism (i)). Actually at these large energies, for $R \leq 1.7$ au, when the crossing region is reached, the whole population of the incident channel should be almost completely absorbed by transitions to Ne singly and doubly excited states (Pedersen *et al* 1978). A rough estimation can be made assuming that impact parameters for R below about 1.7 au do not contribute any more to the $\text{Na}(3s \rightarrow 3p)$ transition. The corresponding cross section should then be reduced by about 30%.

Figure 10. Total Na*(3p) excitation cross section. Experiment: ◆◆◆, Olsen *et al* (1977); theory: ———, Gross *et al* (1978); — — —, Manique *et al* (1977); ———, this work mechanism (ii) Ca 2.

The polarisation of the Na(3s → 3p) radiation has been calculated from the formula

$$P_{23\text{Na}}(3^2\text{S}_{1/2}-3^2\text{P}_{3/2}) = 1.09 \frac{81(\sigma_0 - \sigma_1)}{427\sigma_0 + 773\sigma_1} \times 100 (\%)$$

given by Manique *et al*, where σ_0 and σ_1 are respectively the excitation cross sections of the levels $3p_0$ and $3p_{\pm 1}$. The shape of the calculated polarisation curve (figure 11) is the same as the experimental one but it is shifted towards higher energy.

Figure 11. Polarisation calculated for mechanism (ii). ———, theory; ◆◆◆, experiments (Olsen *et al*).

Returning to the interpretation of the low energy cross section, it must be noticed that the experimental curve of Mecklenbrauck *et al* exhibits a small bump for $20 \text{ eV} < E_{\text{CM}} < 40 \text{ eV}$. All the calculations performed within the framework of mechanism (i), even including the first $3s\sigma''g''\Sigma$ state of the A series, and the rotational coupling between $3s_{\text{Na}}-3p_{\text{Na}}$, do not reproduce this bump. Actually the cross section for mechanism (i) vanishes at the threshold (table 2). In contrast, it has been found that the mechanism (ii) has a non-vanishing cross section at this threshold (table 2) which indicates that the direct radial coupling between $3s_{\text{Na}}-3p_{\text{Na}}$ would be responsible for the

Table 2. The Na(3p) cross section at the threshold: (1) in the 9Σ and Π state model of the mechanism (i), (2) in the six-state model of the mechanism (ii).

E_{CM} (eV)	$\sigma_{Na(3p)}(\text{\AA}^2)$		
	Exp Mecklenbrauck <i>et al</i>	(1)	(2)
40	0.002	0.0007	0.0012
60	0.01	0.01	0.0035
100	0.08	0.08	0.0057

observed bump near threshold. This assumption is limited by the confidence one can have in the use of the impact-parameter method at these low energies.

4. Conclusion

The excitation of the Na(3p) resonance line in the Na–Ne collisions was interpreted using two different models: at low energy, excitation is viewed as taking place via two successive curve crossings located at short internuclear distance whereas at high energy the excitation mechanism switches to a direct transition between the relevant atomic states. The reasonable agreement between present calculations and experiment for both types of mechanism gives solid foundations to the qualitative model, in particular for mechanism (i) for which it is the first calculation. The remaining discrepancies are thought to have different origins for the two mechanisms. A number of additional channels involving two $2p_{Ne}$ excited electrons can be invoked to give a better description of mechanism (i). Concerning mechanism (ii) the inaccuracy of the potential energies and couplings at intermediate and large internuclear distances should be at the origin of the remaining discrepancies.

The present model can be extended to other alkali–rare-gas collisions as well as alkali-earth-ion–rare-gas collisions, as already done for mechanism (ii) by Manique *et al* and Nielsen *et al*.

For mechanism (i) it is interesting to extrapolate the knowledge acquired in the present quasi-symmetric system to very asymmetric systems (i.e. Na–He) which are qualitatively governed by a similar correlation diagram. In a real symmetric system, due to u–g properties there is no interaction at the $3s\sigma_g$ – $4f\sigma_u$ crossing. For a slightly asymmetric system such as the present Na–Ne collision, the underlying u–g symmetry renders weak enough (Sidis *et al* 1977) the interaction at such quasi u–g crossings (C crossing in figure 1) thus allowing both Ne and Na excitation in the present case. This argument completely disappears for very asymmetric systems. The interaction at the C crossing is thus expected to be much stronger. The corresponding large avoidance of the C crossing is thought to be responsible for the much weaker excitation of the noble gas partner (Mecklenbrauck *et al* 1977, Fayeton *et al* 1976).

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References

- Anderson R W, Aquilanti V and Herschbach D R 1969 *Chem. Phys. Lett.* **4** 5-8
Bagus P S, Liu B, McLean R D and Yoshimine M 1971 *IBM Research Publications* **14** 748
Bates D R and McCarroll R 1958 *Proc. R. Soc. A* **245** 175
Brenot J C, Dhuicq D, Gauyacq J P, Pommier J, Sidis V, Barat M and Pollack E 1975a *Phys. Rev. A* **11** 1245-66
— 1975b *Phys. Rev. A* **11** 1933-45
Fayeton J, Andersen N and Barat M 1976 *J. Phys. B: Atom. Molec. Phys.* **9** L149-52
Gaussorgues C, Piacentini R D and Salin A 1975 *Comput. Phys. Commun.* **10** 223-33
Gauyacq J P 1978a *J. Phys. B: Atom. Molec. Phys.* **11** 85-113
— 1978b *J. Phys. B: Atom. Molec. Phys.* **11** L217-22
Gordon R G 1969 *J. Chem. Phys.* **51** 14-25
— 1971 *Math. Comput. Phys.* **10** 81-109
Gross E K U, Horbatsch M and Dreizler R M 1978 *Z. Phys. A* **285** 353-6
Kempter V, Kübler B and Mecklenbrauck W 1974 *J. Phys. B: Atom. Molec. Phys.* **7** 2375-81
Kessel Q C and Fastrup B 1973 *Case Studies in Atomic Physics* vol 3 (Amsterdam: North-Holland) pp 137-213
Kubach C and Sidis V 1976 *Phys. Rev. A* **14** 152-61
Lichten W 1967 *Phys. Rev.* **164** 131-45
Manique J, Nielsen S E and Dahler J S 1977 *J. Phys. B: Atom. Molec. Phys.* **10** 3271-81
Masnou-Seeuws F, Philippe M and Valiron P 1978 *Phys. Rev. Lett.* **41** 395-8
Mecklenbrauck W, Schön J, Speller E and Kempter V 1977 *J. Phys. B: Atom. Molec. Phys.* **10** 3271-81
Nielsen S E and Dahler J S 1976 *J. Phys. B: Atom. Molec. Phys.* **10** 1723-33
Olsen J Ø, Andersen N and Andersen T 1977 *J. Phys. B: Atom. Molec. Phys.* **10** 1723-33
Olsen J Ø, Andersen T, Barat M, Courbin-Gaussorgues Ch, Sidis V, Pommier J, Agusti J, Andersen N and Russek A 1979 *Phys. Rev. A* **19** 1457-84
Pedersen E H, Wahnnon P, Gaussorgues C, Andersen N, Andersen T, Bahr K, Barat M, Cocke C L, Olsen J Ø, Pommier J and Sidis V 1978 *J. Phys. B: Atom. Molec. Phys.* **11** L317-21
Roothaan C C J 1951 *Rev. Mod. Phys.* **23** 69-89
Schneiderman S B and Russek A 1969 *Phys. Rev.* **181** 311-21
Sidis V, Stolterfoht N and Barat M 1977 *J. Phys. B: Atom. Molec. Phys.* **10** 2815-39
Smith F T 1969 *Phys. Rev.* **179** 111-22
Stern B, Gauyacq J P and Sidis V 1978 *J. Phys. B: Atom. Molec. Phys.* **11** 653-66
Taulbjerg K and Briggs J S 1975 *J. Phys. B: Atom. Molec. Phys.* **11** 1895-908
Thorson W R and Delos J B 1978 *Phys. Rev. A* **18** 117-34
Tolk N, Tully J C, White C W, Kraus J, Monge A A, Simms D L, Robbins M F, Neff S H and Lichten W 1976 *Phys. Rev. A* **13** 968-84