Impact-parameter dependence of Na(3s $\rightarrow$ 3p) excitation in Na–Ne collisions

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Abstract. A combined experimental and theoretical investigation of the impact-parameter dependence of Na(3s $\rightarrow$ 3p) excitation in 1–10 keV Na–Ne collisions is presented. Two different mechanisms are shown to account for the features observed in the Na(3p) excitation. At low collision energies, the excitation takes place at well localised molecular curve crossings. At high energies, direct excitation at larger impact parameters dominates.

Two experimental groups have recently measured the total cross section for Na(3s $\leftarrow$ 3p) emission in Na–rare-gas collisions. The low energy region from about 1 keV and down to threshold was covered by Mecklenbrauck *et al* (1977), who interpreted their results in terms of molecular curve crossings (mechanism (i)). High-energy measurements (0.7–50 keV) were performed by Olsen *et al* (1977). Manique *et al* (1977) interpreted theoretically the high-energy excitation as due to the direct electrostatic interaction (mechanism (ii)) between the Na valence electron and the rare-gas atom.

For the Na–Ne system, the Na(3p) emission cross section exhibits two maxima, one at low and one at high energy, located near 0.5 and 15 keV, respectively. Gaussorgues *et al* (1977) suggested that the Na(3s $\rightarrow$ 3p) excitation is induced by both types of excitation mechanisms, (i) and (ii), dominating at low and high energies, respectively. The crucial test of this interpretation can be obtained by an analysis of the impact-parameter (*b*) dependence of the excitation probability since it should be very different for the two pictures. This test is the aim of this letter.

Using a diabatic state correlation diagram shown in figure 1, we see that the molecular excitation, mechanism (i), may take place in the following way: the strong promotion of the 4f σ orbital and the subsequent one-electron transitions at 4f σ –n1 σ

Figure 1. Diabatic potential curves for the $\text{Na}(3s \rightarrow 3p)$ excitation, calculated as described in the text. The curves are referred to the $x^2\Sigma^+$ incident diabatic state. The A series corresponds to excitation of one $4f\sigma$ electron, the B series to excitation of Na. The C series (excitation of two $4f\sigma$ electrons) has been omitted for clarity. In the A series, the four states selected for the calculation of the $\text{Na}(3p)$ excitation are indicated by heavy lines. The first state of the A series does not contribute significantly to the excitation because of the quasi u-g character of the crossing.

MO crossings give rise primarily to Ne excitation (A series). However, on the way out, this series crosses the B series which, in turn, populates the $\text{Na}(3p)$ channel. (Similar mechanisms involving two-electron transitions will also populate the Na^*-Ne^* , $\text{Na}^{**}-\text{Ne}$ and $\text{Na}-\text{Ne}^{**}$ channels). At *low-energy* this two-step excitation mechanism will show a pronounced impact-parameter threshold at the internuclear distance at which the molecular ground state x crosses the A series (Kempter *et al* 1974, Fayeton *et al* 1976). At high energy, mechanism (ii) is expected to become efficient according to the Massey adiabatic criterion. This *high-energy* mechanism, which may operate at large impact parameters, was initially invoked by Nielsen and Dahler (1976).

In order to get an overall picture of the excitation processes at 1–2 keV, differential cross sections (DCS) have been measured in Orsay by the time-of-flight (TOF) technique (figure 2). The TOF spectra displayed the importance of the one- and two-electron excitations in neon, but the energy resolution was not sufficient to resolve the $\text{Na}(3p)$ excitation. The impact-parameter information needed to test the suggested hypothesis was obtained in Aarhus by detection of scattered sodium atoms in coincidence with $\text{Na}(3s \leftarrow 3p)$ photons emitted perpendicular to the scattering plane. The transition region from mechanism (i) to (ii), 2–10 keV, was studied (figure 3(a)) in the reduced angular range $\tau = 0.5\text{--}30$ keV deg (b equal to 1.1–2.8 au). The impact parameter was evaluated from the scattering angle using the Na–Ne potential calculated as reported below. The product of the solid angle and efficiency factors for the photon detection system used for the absolute calibration of the excitation cross sections were found by normalising total photon yields to total excitation cross sections with a claimed

Figure 2. Relative DCS at 2 keV. The three labels *a*, *b* and *c* correspond to zero-, one- and two-electron excitation of the Ne atom. The dotted curve is the total differential cross section, $a + b + c$. Also shown is the Na(3p) DCS (*d*) obtained from the coincidence experiment by multiplying the total cross sections by the probabilities of figure 3(a).

uncertainty of 30% (Olsen *et al* 1977). The consistency of the probability and impact-parameter scale was checked by integrating the excitation probabilities over impact parameters to obtain the total excitation cross section, which was reproduced to within 30%. Figure 3(a) shows that at 2 keV there is a well localised impact-parameter threshold for excitation, giving direct evidence for the fact that here only mechanism (i) is efficient; with increasing energy, excitation gradually shows up at larger impact parameters, indicating the onset of the direct mechanism (ii).

Figure 3. Transition probabilities for Na(3s $\rightarrow$ 3p) excitation plotted against impact parameter. (a) Experimental results at 2 keV ($\bullet$), 4 keV ($\times$) and 10 keV ($\circ$). (b) Theory; mechanism (i): 1 keV, full curve, $\times 2$; mechanism (ii): at 2 keV ($\bullet$), 4 keV ($\times$), and 10 keV ($\circ$), $\times \frac{1}{3}$. The multiplication factors assure agreement with the measured total cross sections at 1 and 10 keV, respectively.

The 2 keV coincidence data are also shown on figure 2. The similar behaviour of the Na(3p) and Ne excitation DCS indicates that both processes are primarily induced at the same internuclear distance as expected for mechanism (i). The deflection functions for the two excitation processes differ very little, even though the product channels differ in energy by about 15 eV. This occurs because the curve crossings at 1.5 au take place at an energy approximately 100 eV above the energy of the separated Na(3s) + Ne system.

Two different theoretical approaches have been used to evaluate the impact-parameter dependence for mechanisms (i) and (ii), respectively.

Mechanism (i). Since the inelastic processes in the Na-Ne collision involve the $4f\sigma$ promotion, the 'frozen-orbital' method (Gauyacq 1978) is appropriate to handle *ab initio* the present diabatic MO crossings. Briefly, the molecular diabatic states are represented by single configurations built from MO expressed as linear combinations of Slater-type orbitals. A self-consistent field calculation of the $(\text{Na-Ne})^+ \times {}^1\Sigma^+$ ground state is used to generate a set of MO down to $R = 2$ au. At smaller distances, in the MO crossing region, the expansion coefficients of the outer orbitals are frozen. Single-configuration states obtained by one- (A series) and two- (C series) electron excitation from the $4f\sigma$ MO as well as single excitation from the $\sigma 3s$ Na (B series) have been considered. Limited configuration-interaction calculations in each subspace of the A and C series have been performed to select the most significant states. The four states of the A series which have the largest interaction (≥ 0.6 eV) with both the incoming $\times {}^2\Sigma$ Na(3s) and outgoing $\text{B } {}^2\Sigma$ Na(3p) channels are selected for the cross section calculations. The six-state close-coupling calculations show important excitation of both Na(3p) and Ne(3p) in the low-energy range. Since the C series have been omitted, the calculations may be uncertain above about 1 keV.

Mechanism (ii). Since the direct excitation mechanism is expected to be important at high energy and large internuclear distances, a perturbed atomic description seems more appropriate here. The computation procedure for the energies and couplings involves single configurations of frozen orthonormalised atomic orbitals of Na and Ne (1s to 3p of each atom). At first sight, the Na(3p) population should only involve the radial and rotational couplings between the 3s, $3p_0$, $3p_{\pm 1}$ Na orbitals. However, Rydberg orbitals centred on the Ne atom, $(\sigma 3s, \sigma 3p, \pi 3p)_{\text{Ne}}$ were also included

Figure 4. Total cross section for Na(3p) emission. Experiment: ●, Olsen *et al* (1977);, Mecklenbrauck *et al* (1977). Theory: +, mechanism (i), ×, mechanism (ii).

in order to take the $3s_{\text{Na}}-3s_{\text{Ne}}$, $3p_{\text{Na}}-3p_{\text{Ne}}$ exchange interaction into account via virtual transitions.

For both mechanisms, the calculated transition probabilities plotted against impact parameter are shown in figure 3(b). There is good agreement between experiment and theory concerning both the location of the peak near $b \simeq 1.5$ au, and the impact-parameter and energy dependence of the transition probability, supporting further the proposed interpretation. The agreement in absolute value is, however, only semi-quantitative.

The low-energy theoretical total cross section compares satisfactorily with the low-energy experimental data, see figure 4. The calculated high-energy total cross section overestimates the experimental data by about a factor of 3, although it is in better agreement with experiment with respect to the location of the maximum and also the magnitude of the cross section than previous theoretical calculations (Manique *et al* 1977). The remaining discrepancy may result from the 'frozen' nature of the orbitals involved in the calculation.

In conclusion, the combined experimental and theoretical results delineate clearly the two proposed $\text{Na}(3s \rightarrow 3p)$ excitation mechanisms. In particular, the impact-parameter dependence of the $\text{Na}(3p)$ excitation demonstrates that well localised curve crossings are mainly responsible for the excitation at low energies. At higher energies, around the maximum in the total cross section, direct excitation at larger impact parameters dominates.

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