Polarization Dependence of Resonant Charge Transfer in Low-Energy Collisions of Na^+ with Laser-Excited $Na^*(3p)$

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Relative differential cross sections for charge-transfer scattering have been measured over the collision energy range $E_{c.m.}=45$–75 eV. With linearly polarized light exciting $Na(3s)$ to $Na^*(3p)$, the dependence of the charge-transfer cross section on the predominant preparation of the Σ or Π excited states of the ionic quasimolecule Na_2^+ has been studied. The results are compared to simple model calculations. It is found that the resonant charge exchange is most probable for the predominant preparation of the $Na_2^+(2\Sigma_{g,u})$ excited states.

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There has been considerable interest in single electron capture for many years. Resonant charge transfer (CT) in the alkali-ion–atom systems has been studied extensively, both for the asymmetric and the symmetric case. For the reaction $Na^+ + Na(3s) \rightarrow Na(3s) + Na^+$ the total cross sections[1] as well as the differential cross sections[2] have been measured. Theoretical models[3] of the charge-transfer process have been developed, in which the oscillation of the electronic charge cloud is considered to be the basic charge-transfer mechanism if the relative velocity of the heavy-particle motion is lower than the mean orbital velocity of the captured electron.

In this work we extend the investigation of the CT reaction by employing the laser optical-pumping technique[4] to a crossed-beam ion-atom scattering experiment.[5,6] This method allows alignment of the electronic charge cloud of the neutral $Na^*(3p)$ prior to the collision and study of the dependence of the CT cross section on the alignment angle of the $3p$ orbital. The reaction investigated can be described as

$$Na^+ + Na^*(3p, |m_l|) \rightarrow Na_2^+(\Lambda) \rightarrow Na^*(3p, |m_l|) + Na^+, \quad (1)$$

where the magnetic substate $m_l = 0$ corresponds to a σ orbital and $|m_l| = 1$ to a π orbital with respect to the axis of the incoming ion beam, while Λ stands for the molecular states Σ and Π. At low collision energies and in the angular range ($E_{c.m.} \times \theta_{c.m.} < 100$ eV deg) studied, inelastic processes[5,6] can be neglected in the investigation of CT because their cross sections are orders of magnitude smaller than the resonant CT process discussed here. The observed differential cross sections for CT will be compared to the results of calculated cross sections based on recently published potential energies[6] for Na_2^+.

Details of the experiment have been presented before,[5,6] so we give here only a brief description. An energy-selected Na^+ beam (150 meV full width at half maximum) crosses a sodium-atom beam at right angles. Sodium atoms which are scattered into a laboratory angle θ_{lab} are detected by a particle multiplier. The detection of scattered ions is inhibited by a retarding field in front of the multiplier. The overall angular resolution is $\Delta\theta_{lab}$ (full width at half maximum) $= 1°$ ($\Delta\theta_{c.m.} = 2°$). The sodium atoms in the scattering center are excited to the $Na^*(3^2P_{3/2}, F=3)$ state by linearly polarized laser light propagating perpendicular to the atomic beam.

Figure 1 shows the measured differential cross sections for the CT reaction at $E_{c.m.} = 45$ eV. The cross section for the ground-state reaction

$$Na^+ + Na(3s) \rightarrow Na(3s) + Na^+$$

shows a pronounced maximum at a scattering angle of $\theta_{c.m.} = 0°$ and decreases smoothly with increasing angle. Since the angular resolution in this experiment is poor, the CT oscillations and the $d\sigma^{CT}(\theta_{c.m.}=0°)/d\Omega = 0$ singularity are averaged out. By subtracting from the scattering signal with light on (I_{on}) the signal with light off (I_{off}) we obtain

$$(I_{on} - I_{off}) \propto \left(\frac{d\sigma^{CT}(3p)}{d\Omega} - \frac{d\sigma^{CT}(3s)}{d\Omega} \right). \quad (2)$$

The difference between the cross sections for the ground-state reaction and the excited-state reaction

$$Na^+ + Na^*(3p) \rightarrow Na^*(3p) + Na^+,$$

shows that the latter is more probable than the former. For these measurements the $Na(3s) \rightarrow Na^*(3p)$ optical pumping was performed with linearly polarized laser light, where the E vector was perpendicular to the primary ion beam. With an es-

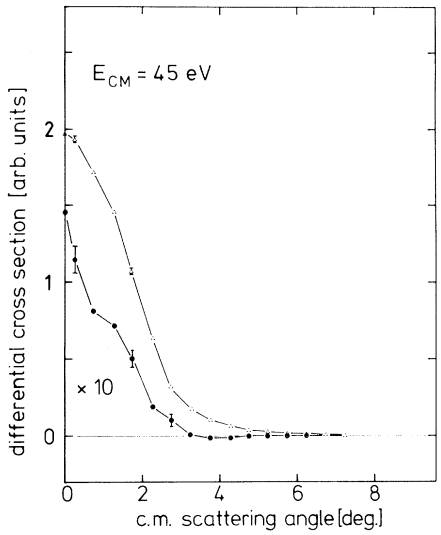

FIG. 1. Differential cross sections for symmetric charge transfer $Na^+ + Na \rightarrow Na + Na^+$. Open triangles, $d\sigma^{CT}(3s)/d\Omega$; solid circles, $d\sigma^{CT}(3p)/d\Omega - d\sigma^{CT}(3s)/d\Omega$.

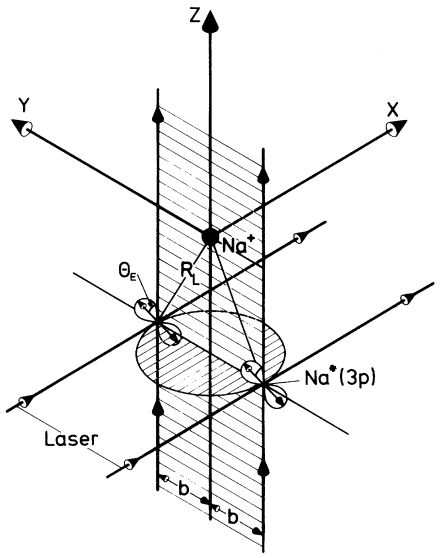

FIG. 2. Experimental collision geometry for the $Na^+ + Na^*(3p)$ process. The z axis is parallel to the incoming Na^+ beam. The $Na(3p)$ orbital is aligned under the angle θ_E relative to the z axis. Two "locking" geometries with same R_L but $y = \pm b$ are depicted and display the averaging due to detection at the scattering angle $\theta_{c.m.} = 0°$.

timated population of the $Na^*(3p)$ state of 10% we obtain $d\sigma^{CT}(3p)/d\Omega = 2d\sigma^{CT}(3s)/d\Omega$.

For further experiments we will detect the neutral-particle signal at a scattering angle of $\theta_{lab} = 0°$ only, thereby averaging over $\theta_{c.m.} = +1°$. Before discussing the results of the polarization studies of the present experiment, we outline briefly the model picture of the inelastic scattering processes developed previously.[5,6] We have found that for the inelastic processes with impact parameters $b \sim 5$ a.u., the quasimolecule Na_2^+ is formed in a "merging" region which is characterized by an effective "locking" radius of about $R_L = 35$ a.u. The atomic $Na^*(3p)$ orbital may be considered to be space fixed for internuclear distances R larger than R_L while for smaller distances the charge cloud is locked to the rotating internuclear axis where the $3p$ orbital correlates to the $2^2\Sigma_{g,u}$ and $1^2\Pi_{g,u}$ states. The order of magnitude of R_L was deduced from measurements[5] of the $3p$ charge-cloud alignment angle prepared asymptotically in order to obtain a maximum preparation of the $1^2\Pi$ and $2^2\Sigma$ excited states of the Na_2^+ quasimolecule formed in the collision.

In Fig. 2 the collision geometry of the present experiment is displayed; the z axis is parallel to the incoming ion beam. For convenience we have shown a situation where the Na^+ is fixed in space at the origin, whereas the $Na(3p)$ atom is moving. The situation in the experiment is different because there the ion is moving. The dynamics, however, are in both cases the same. The laser beam travels perpendicular to the ion beam and the angle between the E vector of the linearly polarized laser light and the z axis is denoted by θ_E. The detection window is $\Delta\theta_{c.m.} = 2°$ around $\theta_{c.m.} = 0°$. Therefore the experiment has axial symmetry with respect to the z axis and averages the polarization dependence of the CT cross section. This is exemplified by two straight-line trajectories of the $Na(3p)$ atom with impact parameter $y = \pm b$. The polarization angle θ_E is equal for both trajectories. For the b and R_L assumed in Fig. 2 we prepare for $y = +b$ predominantly a $Na_2^+(1\Pi)$ state and for $y = -b$ predominantly a $Na_2^+(2\Sigma)$ state. The result of the averaging procedure shows that an anisotropy remains if the cross section for CT is larger for the $2\Sigma_{g,u}$ states than for the $1\Pi_{g,u}$ states or vice versa. Then one expects a maximum in the scattered intensity at $\theta_E = 0°$ or $\theta_E = 90°$, respectively.

In Fig. 3 the measured polarization dependence is shown for the difference of the CT cross sections as given by Eq. (2). The cross section $\sigma(3s)$ is independent of the polarization; therefore Fig. 3 displays the polarization dependence of $\sigma(3p)$. The measurements show extrema exactly at $\theta_E = 0°$ and $\theta_E = 90°$. The maximum at $\theta_E = 0°$, combined with the prediction of the locking model that this maximum corresponds to the predominant preparation of 2Σ states, is in agreement with semiclassical cal-

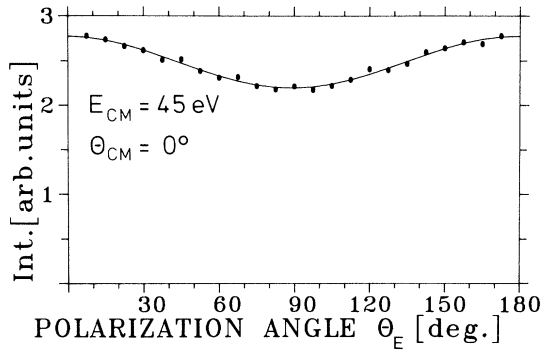

FIG. 3. Polarization dependence of the charge-transfer cross section; solid circle, experiment; solid line, $\cos\theta_E$ fit. $\theta_E = 0°$ and $\theta_E = 90°$ give predominant preparation of $Na_2^+(2\Sigma)$ and $Na_2^+(1\Pi)$, respectively.

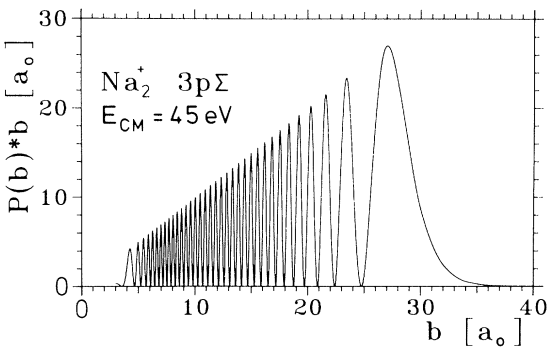

FIG. 4. Theoretical electron-capture probability multiplied by the impact parameter b and displayed as function of b.

culations of the total cross section. By use of straight-line trajectories we obtain from the known $V_{g,u}$ potential energy curves[6] the total cross section[1]

$$\sigma(E) = 2\pi \int_0^\infty [P(b,E)\ b]\, db, \tag{3}$$

$$P(b,E) = \sin^2(\eta/2), \tag{4}$$

$$\eta(b,E) = 2(\mu/2E)^{1/2} \int_b^\infty \{[V_g(R) - V_u(R)]/(1 - b^2/R^2)^{1/2}\}\, dR, \tag{5}$$

where μ is the reduced mass, E the collision energy, b the impact parameter, and R the internuclear distance.

Figure 4 shows as an example the electron-capture probability of Na^+ as a function of the impact parameter b if the system proceeds through the $Na_2^+(2\Sigma_{g,u})$ excited states. The weighted theoretical probability $P(b)\,b$ displays the contribution of each oscillation to the total cross section, which is the total area under this curve. $P(b)\,b$ has its maximum at $b = 27$ a.u., whereas the probabilities for the $Na_2^+(1\Pi_{g,u})$ excited state and for the $Na_2^+(1\Sigma_{g,u})$ ground state peak at $b = 20$ a.u. and $b = 17.5$ a.u., respectively. The energy dependence of the total cross section is shown in Fig. 5 for all three potentials. At $E_{c.m.} = 45$ eV the calculated integrated CT cross sections have the magnitudes $\sigma(3s) = 675a_0^2$, $\sigma(3p,\Sigma) = 1600a_0^2$, and $\sigma(3p,\Pi) = 950a_0^2$.

In order to obtain an estimate for R_L we have averaged the projections of the asymptotically prepared p orbital onto Σ and Π states as indicated in Fig. 2. The resulting anisotropy has then been averaged over the impact parameters. The contribution of each impact parameter is given by the angular resolution of the experiment. The computation gives a $\cos\theta_E$ dependence. The best agreement between the observed ratio of the maximum to minimum cross section as a function of θ_E depicted in Fig. 3 and the calculations is a "locking" radius $R_L > 45$ a.u. .

The merging region for CT collisions thus extends to larger internuclear distances than for the $Na^+(3p)$ inelastic collisions. From Fig. 4 we see that for the electron transfer impact parameters up to $b \sim 30$ a.u. contribute significantly, whereas for the inelastic collisions the dominant impact parameters are $b = 4.8$–5.6 a.u. with $R_L < 35$ a.u. Detailed semiclassical calculations,[7] where the time-dependent Schrödinger equation for the electronic motion is solved, show that only for the case $b \ll R_L$ is the "locking" radius R_L independent of b. For b in the same order of magnitude as R_L, R_L

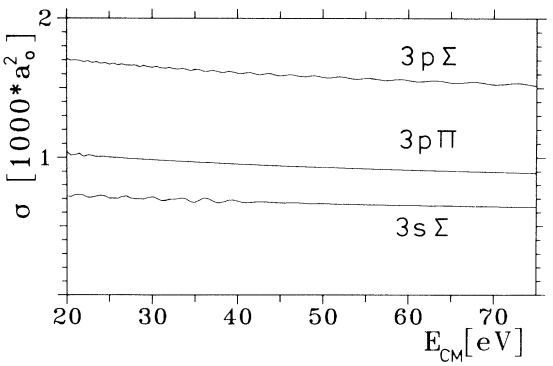

FIG. 5. Calculated energy dependence of the total charge-transfer cross section in $Na^+ + Na(3p, 3s)$ collisions.

is dependent on the impact parameter. This is in qualitative agreement with the present experimental results. For a quantitative comparison the experiment warrants a rigorous quantum-mechanical calculation because the differential cross section is strongly peaked at small scattering angles. This corresponds to a range of comparitatively large impact parameters where interference effects as a result of the heavy-particle motion play a significant role. The alignment dependence of the CT cross section appears to be an interesting test case for dynamical calculations, since reliable potential curves and nonadiabatic coupling elements are available.

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