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Strong temperature dependence of laser-enhanced charge transfer in collisions of sodium clusters with sodium atoms

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We have performed a combined experimental and theoretical study of the charge transfer for 5-keV Na_n^+ cluster-ion collisions with Na atoms in their ground and laser-excited states. The theoretical analysis of the laser-enhanced charge-transfer probability, based on a self-consistent treatment of both charge-transfer and collision-induced fragmentation, shows a crucial dependence on the energy content of the Na_n^+ clusters before the collision. Quantitative information on this energy is obtained by comparing experimental data with theoretical results. [S1050-2947(99)50504-0]

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Charge transfer (CT) is one of the fundamental yet still challenging processes in atomic collision physics [1]. In addition to the related electronic transitions, new interactions occur if the collision partners possess other internal degrees of freedom. Clusters [2] provide a particularly interesting case: with great flexibility they allow one to investigate electronic transitions as well as their coupling to the nuclear dynamics in aggregates having a large but finite number of degrees of freedom. Only recently has it become clear that in such systems the initial internal energy (temperature) of the clusters is of decisive importance for the understanding of a variety of phenomena; e.g., the optical response [3], fusion barriers in cluster-cluster collisions [4], collisional energy transfer [5], Coulombic fission [6], and shell structure [7]. Under such conditions, experimental collision studies using laser-optically manipulated partners are expected to be of great value; as has already been exploited in atomic ion collision studies (for a review cf., e.g., [8]), they permit us to introduce a range of well-defined changes in the initial electronic configuration and, thus, the energy content without having to modify the projectile-target combination or energy. A newly developed theoretical approach allows us to cope with such situations, namely, the nonadiabatic quantum molecular dynamics (NA-QMD) [9,10]. This theory treats the classical atomic motion simultaneously and self-consistently with the electron dynamics by combining molecular dynamics with *time-dependent* density-functional theory [11] in the Kohn-Sham (KS) formulation [9]; it describes adiabatic as well as nonadiabatic collisions, including the regime where both electronic and vibrational excitations occur [5,10].

In this Rapid Communication we report on an experimental study of CT in cluster ion-atom collisions with a target in a laser-excited state as well as in its electronic ground state, and a theoretical treatment of this system using the NA-QMD approach. The system under study is

$$Na_n^+ + Na(3s) \rightarrow Na_n + Na^+, \tag{1a}$$

$$Na_n^+ + Na(3p) \rightarrow Na_n + Na^+, \tag{1b}$$

with cluster size $n = 1, \ldots, 4$. The experiment yields a strong n dependence of the laser-induced enhancement of the CT probability. The results provide a kind of ''cluster thermometer'': Complementary to the extraction of the *electronic* temperature of large clusters [7], our analysis, based on a simultaneous and self-consistent treatment of CT and ensuing fragmentation, gives direct information on the *rovibrational* energy content of the clusters before the collision.

In the experiment, a Na_n cluster beam is produced by heating Na in an oven and expanding the vapor under He flow through an orifice of about 50 μm diameter into vacuum. Clusters are postionized by 80-eV electrons from a filament placed in front of the orifice; thus, the clusters are ''hot.'' Cluster ions are extracted with a voltage of 4 and 5 kV into a beam guide system; after a flight time of about 3 μs a Wien filter selects the desired mass. After collimation to $\pm 0.15°$ the beam is cleaned of neutralized ions by an electrostatic deflection system. In the interaction zone it is crossed at right angles by a laser beam and a Na atom beam under single-collision conditions; this region is free of static fields. The linearly polarized laser light originates from a single-mode cw Ar ion/dye laser combination (Coherent); it is tuned to the $Na(3s)^2S_{1/2}(\overline{F}=2) \rightarrow Na(3p)^2P_{3/2}(F=3)$ transition (589 nm) using an external Na stabilization oven. Due to the hyperfine interaction, the laser light excites an incoherent mixture of Σ and Π states in the Na target; e.g., for the electric vector parallel to the cluster-ion beam (z) axis, the relative Σ and Π populations are 5/9 and 4/9, respectively; for the electric vector perpendicular to the z axis, these values are 2/9 and 7/9, respectively. Under stationary laser pumping conditions, the $3p$ population is 12–15% of the Na beam [12]. It has been verified that the laser power employed in this experiment ($\sim 100\,\mathrm{mW/cm^2}$) is much too low to cause any noticeable heating or fragmentation of the cluster-ion beam. After the interaction region, the remaining cluster ions are deflected from the beam. The neutralized clusters continue for a distance of 50 cm into a channeltron detector; we discriminate against neutral fragments from collision-induced breakup by placing a small aperture in

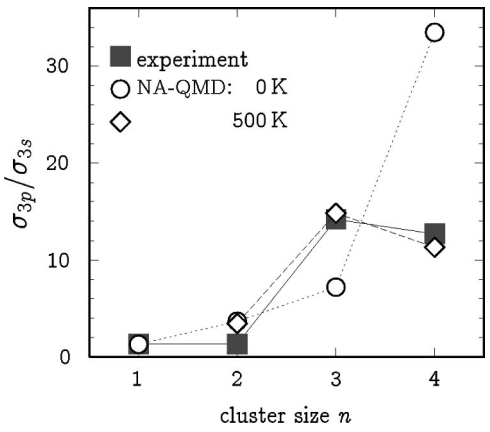

FIG. 1. Total cross-section ratio for CT in collisions $Na_n^+ + Na(3s,3p) \rightarrow Na_n + Na^+$ $(n=1,\ldots,4)$ at an energy of $E_{lab} = 5$ keV. The experimental data (full squares) are compared with theoretical results obtained from NA-QMD calculations (open symbols) for two initial temperatures of the clusters. The thin lines are only to guide the eyes.

front of this detector, which rejects particles having angles $> \pm 0.15°$ relative to the primary beam direction.

The laser-enhanced CT probability at 5-keV collision energy is shown in Fig. 1. The enhancement σ_{3p}/σ_{3s} is particularly noticeable for Na_3^+ and Na_4^+ cluster-ion impact; similar results are obtained at 4-keV energy. We have also studied the influence of an initial $Na(3p)$ alignment by varying the linear polarization direction of the laser light. As in the ion-atom case [13] the effect was found to be smaller than 5%.

To understand the strong dependence of the CT cross-section ratio on the cluster size n, the collisions have been analyzed theoretically within the NA-QMD framework. Let us first consider the test case of the ion-atom scattering $Na^+ + Na(3s,3p)$ [14], where one can also compare the results with other experiments [15]. The calculated absolute value of the total cross section $\sigma_{3s} = 305 a_0^2$ is in reasonable agreement with the experimental value $\sigma_{3s} = 335 a_0^2$ of [15] with a_0 the Bohr radius. The obtained theoretical ratio of the integral CT cross sections $\sigma_{3p}/\sigma_{3s} = 1.28$ agrees very well with the present experiment of $\sigma_{3p}/\sigma_{3s} = 1.34$ (see Fig. 1).

In the case of cluster collisions the theoretical analysis is much more involved because one has to (i) treat the CT in a real *many-electron system*, (ii) take into account simultaneously the *fragmentation* of the clusters because the experiment discriminates against fragmentation, (iii) consider for a given impact parameter many different *orientations* of the cluster with respect to the beam axis, in order to obtain orientation-averaged quantities, (iv) consider that the clusters in the beam do have an internal energy E_{int} or *temperature*, which in the present experiment is unknown.

For a systematic discussion of these points let us first introduce a so-called *primary* CT probability P_{CT}^{prim}. For a single-collision event, it will be defined as the probability for electron transfer from the target atom to the cluster projectile independent of the further evolution of the cluster (i.e., disregarding fragmentation processes) [16]. In many-electron systems, the calculation of those quantities is quite demanding [17–19]. Instead of one-active electron approximations (as, e.g., applied in [17]), projections of Slater determinants constructed from single-particle KS functions are used to calculate P_{CT}^{prim} [19] in analogy to former time-dependent Hartree-Fock calculations for atomic two-electron systems [18].

Next, since in the experiment only nonfragmented neutral clusters are detected, it is mandatory to exclude in the theoretical analysis all those events where fragmentation will occur. This process, collisionally induced by energy transfer into nuclear as well as into electronic degrees of freedom [20] including electron-vibration coupling, is automatically contained and correctly described by the NA-QMD theory [5,10]. Statistical evaporation, however, which takes place on a microsecond time scale cannot be traced easily by molecular dynamics. To allow also for statistical evaporation we consider the calculated total electronic and vibrational excitation energy of the cluster after the collision. If this quantity exceeds the dissociation threshold evaporation is assumed; these events are also excluded from the so-called *final* CT probability P_{CT}^{final}.

Further, for each impact parameter b about 100 molecular-dynamics calculations with different (random) orientations of the cluster with respect to the beam axis have been performed. One obtains the orientation-averaged primary and final CT probabilities $P_{CT}^{prim}(b)$ and $P_{CT}^{final}(b)$ as well as the fragmentation probability $P_{frag}(b)$. Total cross sections are then obtained by a b-weighted integration over about 30 impact parameters.

Finally, the calculations with zero temperature clusters have been performed with geometrical ground-state structures obtained by steepest descent (equilateral Na_3^+, rhombic Na_4^+), which agree very well with Hartree-Fock calculations [21]. Finite-temperature calculations are done using rovibrationally excited clusters with a fixed (kinetic plus potential) internal energy E_{int}; for the small clusters studied here, electronic degrees of freedom do not play any role [7,22]. The clusters are prepared by equilibrating the hot clusters over a few picoseconds in adiabatic QMD calculations [9]. For convenience, we relate the internal energy E_{int} to a ''temperature'' T by $E_{int}/f = kT$ with $f = 3n-3$ regarding vibrational *and* rotational degrees of freedom to be excited in these small systems.

Let us first discuss the results obtained with zero-temperature clusters $T = 0$ K (''cold''). In the left column of Fig. 2 the primary CT probabilities $P_{CT}^{prim}(b)$ are shown. As expected, for all systems the probability for the excited target $Na(3p)$ exceeds the one for $Na(3s)$, in particular for large impact parameters. However, at small b the reaction mechanism is dominated in all systems by fragmentation; for Na_4^+ collisions, this is shown in the left part of Fig. 3. Independent of the target state the fragmentation probability $P_{frag}(b)$ is nearly 1 for impact parameters below the cluster size $(\sim 6a_0)$. Consequently, only large impact parameters contribute to the final CT probabilities $P_{CT}^{final}(b)$; see lower part of Fig. 3. Note, however, that the ratio of the integrated cross sections is by far too large for $n=4$ as compared to experiment; moreover, the calculated n dependence is in qualitative disagreement with the experimental data (see Fig. 1; for absolute values see Table I).

Next, we have repeated the analysis by taking into account and successively increasing the initial internal energies

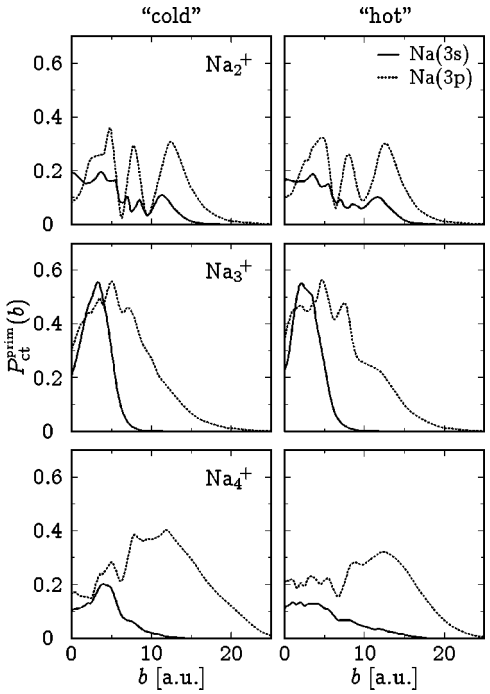

FIG. 2. Primary CT probability $P_{\mathrm{CT}}^{\mathrm{prim}}(b)$ as a function of the impact parameter b for the collisions $\mathrm{Na}_n^+ + \mathrm{Na}(3s,3p) \rightarrow \mathrm{Na}_n + \mathrm{Na}^+$ for $n=2,\ldots,4$ (from top to bottom) at $E_{\mathrm{lab}}=5$ keV. The initial temperatures of the clusters are $T=0$ K (''cold'' clusters, left column) and $T=500$ K (''hot'' clusters, right column), respectively.

E_{int} of the clusters. At a temperature $T=500$ K (''hot'') an overall agreement with the experimental ratios is obtained; see Fig. 1.

This behavior may be understood in full microscopic detail. A finite temperature can considerably influence the electronic transitions (i.e., increase or decrease the primary CT probabilities) and promotes the fragmentation process. The competition between (or the support of) both effects may increase (or decrease) the total final CT cross sections.

For the most sensitive case Na_4^+, details of this interplay are demonstrated in Figs. 2, 3, and 4. As compared to the

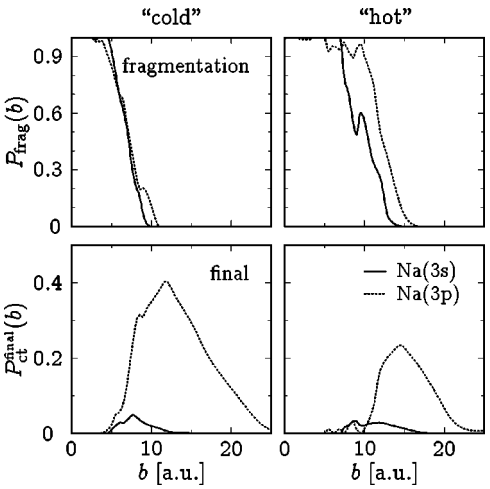

FIG. 3. Impact-parameter dependence of the fragmentation probability $P_{\mathrm{frag}}(b)$ (upper panel) and the final CT probability $P_{\mathrm{CT}}^{\mathrm{final}}(b)$ (lower) for the collisions $\mathrm{Na}_4^+ + \mathrm{Na}(3s,3p) \rightarrow \mathrm{Na}_4 + \mathrm{Na}^+$ at $E_{\mathrm{lab}}=5$ keV for the same two temperatures of Na_4^+ as in Fig. 2.

TABLE I. Total CT cross sections obtained from $P_{\mathrm{CT}}^{\mathrm{final}}(b)$ for collisions $\mathrm{Na}_n^+ + \mathrm{Na}(3s,3p) \rightarrow \mathrm{Na}_n + \mathrm{Na}^+$ at $E_{\mathrm{lab}}=5$ keV.

T (K)	Cluster	σ_{3s}/a_0^2	σ_{3p}/a_0^2	σ_{3p}/σ_{3s}
0	Na_2^+	43	157	3.6
	Na_3^+	25	178	7.1
	Na_4^+	10	340	34
500	Na_2^+	46	159	3.4
	Na_3^+	13	187	14
	Na_4^+	15	166	11

$T=0$ K case, the primary CT probability is considerably increased in the interesting range of impact parameters (i.e., $b \gtrsim 10a_0$) for Na($3s$) collisions, whereas it is decreased for Na($3p$) collisions; cf. Fig. 2. A qualitative explanation of these changes can be deduced from the density of the KS single-particle levels presented in Fig. 4. Whereas the singly occupied KS level of the cluster at $T=0$ K is shifted towards the atomic $3s$ level at $T=500$ K, the more resonant character in the Na($3p$) $T=0$ K case is disturbed to some extent by smoothing out the corresponding $T=500$ K. In both cases, the temperature considerably increases the fragmentation probability $P_{\mathrm{frag}}(b)$; cf. Fig. 3. The changes in the final CT probabilities, however, are qualitatively different for Na($3s$) and Na($3p$) collisions, respectively. The cross sections in the Na($3s$) case increase by a factor of 1.5, whereas σ_{3p} is drastically reduced from $340a_0^2$ to $166a_0^2$ (see Table I) leading, altogether, to a ratio of 11 (instead of 34), in excellent agreement with experiment.

Just the opposite changes are observed in the (less sensitive) Na_3^+ collisions. Here the initial temperature increases the primary Na($3p$) CT probabilities at large impact parameters, whereas the Na($3s$) probability remains nearly unaffected (Fig. 2). As a consequence, the increased fragmentation probability decreases drastically the final cross section σ_{3s}, whereas σ_{3p} is even slightly increased by electronic effects. Altogether, this leads to a twice as large ratio as compared to the $T=0$ K case (Table I).

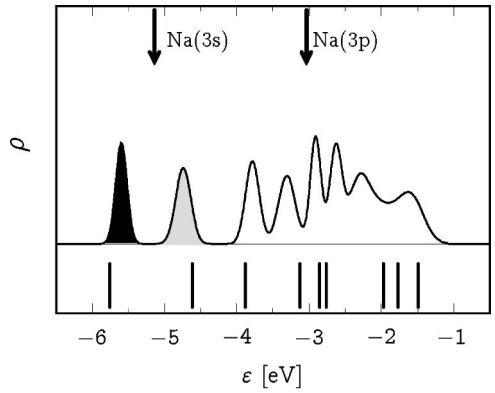

FIG. 4. Electronic density of single-particle states ρ of Na_4^+ for $T=500$ K. It has been obtained by fitting Gaussians to the distribution of stationary KS levels from the 100 initial ionic configurations. The arrows and vertical lines mark the ionization potentials of Na($3s$,$3p$) and the electronic levels of the cluster at zero temperature, respectively. The doubly and singly occupied single-particle levels of the cluster are indicated by the black and gray shaded peaks, respectively.

Finally, in dimer collisions both electronic transitions and fragmentation remain practically unaffected by temperature. In this case, the corresponding internal energy at $T=500$ K is too small to induce significant changes in the electronic structure for the transfer and, in addition, is far below the dissociation threshold of the collision-produced closed-shell system Na_2.

In conclusion, the peculiar n-dependence of the experimental CT cross-section ratio σ_{3p}/σ_{3s} is the result of a sensitive interplay between electron transfer and cluster fragmentation. Both processes are extremely sensitive to the energy content of the primary clusters. Studies involving laser-excited targets may therefore provide a kind of ''cluster thermometer.''

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