Rapid Note

Charge transfer in cluster-atom collisions

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Abstract. Charge transfer in collisions $Na_n^+ + Cs \longrightarrow Na_n + Cs^+$ ($4 \leq n \leq 11$) is investigated theoretically within a microscopic framework. It is shown that an understanding of the measured charge transfer cross-sections can be obtained only if the competing reaction channels (electronic excitations and fragmentation) are treated simultaneously and, in addition, if the initial temperature of the clusters in the beam is taken into account. The energy dependence of the cross-sections is predicted. An exotic charge transfer channel producing Cs^- is found to have a finite probability.

PACS. 34.70.+e Charge transfer – 36.40.Qv Stability and fragmentation of clusters – 31.15.Qg Molecular dynamics and other numerical methods

Charge transfer represents one of the fundamental atomic interactions. In the last decade, considerable progress has been made in the understanding of charge transfer mainly for two cases: elementary ion-atom reactions [1] and complex ion-surface interactions [2]. Recently, there has been a flurry of activity aiming at closing the gap between these two limiting cases by investigating the intermediate case of ion-cluster collisions [3–18]. In general, the fundamental events accompanying cluster collisions include simultaneous and mutually coupled electronic transitions (charge transfer, excitation, ionization) and energy transfer in nuclear (or core) degrees of freedom (vibrations, rotations, fragmentation). These take place simultaneously and involve a moderate to large, but finite, number of electronic and nuclear degrees of freedom. In particular, collision-induced dissociation (CID) competes with charge transfer (CT) in such collisions.

In one of the first experiments with mass-selected cluster beams CT and CID were investigated for $Na_n^+ + Cs$ [3,4] and $K_n^+ + Cs$ [4] collisions. An important result of these experiments is the measurement of the CT cross-section for the neutralization of the parent cluster ion,

$$Na_n^+ + Cs \longrightarrow Na_n + Cs^+, \qquad (1)$$
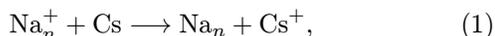
by detecting the neutral products associated with process (1) and distinguishing them from those originating from CID. Subsequent experimental studies of CT in collisions of cluster cations with atoms [5–10], molecules [7] and clusters [9,11] produced a considerable amount of

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data. Multiple CT processes accompanied by fragmentation have been observed in collisions of highly charged ions with fullerenes [12,13] and sodium clusters [14].

The impressive experimental progress is complemented by a number of theoretical descriptions of CT reactions in cluster collisions. In reference [4], a two-state model of (near) resonant CT is presented. Classical barrier models [15,16] have been applied to distant collisions of C_{60} with highly charged ions. Semi-microscopic descriptions of CT, which are based on the jellium approximation [17] or on phenomenological single-particle potentials [18], have also been suggested. However, the combined description of CT *and* fragmentation or, more generally, a simultaneous treatment of electronic *and* nuclear degrees of freedom in non-adiabatic cluster collisions remained an unsolved problem. But, as we show in this letter, it is precisely the coupled electronic-nuclear dynamics and the competition between CT and fragmentation that plays a keyrole in understanding and explaining the measured CT cross-sections [3,4] in collision process (1).

In what follows we present a fully microscopic analysis of CT and fragmentation in $Na_n^+ + Cs$ collisions using the so-called non-adiabatic quantum molecular dynamics (NA-QMD) developed recently [19]. This dynamics describes the classical atomic motions simultaneously and self-consistently with the electronic transitions in atomic many-body systems. It combines molecular dynamics with time-dependent density functional theory [20] in which the Kohn-Sham formalism is implemented within the time-dependent local density approximation. The LCAO ansatz

for the Kohn-Sham orbitals leads to a set of coupled differential equations for the time-dependent coefficients which determine the time evolution of the electronic density as a function of the classical motion of the atoms. Simultaneously, Newton's equations of motion with explicitly time-dependent forces are solved. This allows for the possible energy transfer between the classical system of the ionic cores and the quantum-mechanical system of the valence electrons. The NA-QMD approach has been used and tested against experimental data in an analysis of kinematically complete correlation measurements of CID [21] and in a general study of the excitation and relaxation mechanisms in atom-cluster collisions over a broad range of collision energies (from eV to MeV) [22]. Here, we apply the same formalism to investigate CT and fragmentation. The details of the procedure used to calculate probabilities of specific electronic transitions defined by the time-dependent electronic density will be given elsewhere [23].

In order to uncover the different physical processes that determine the absolute cross-section of the CT reaction (1), we have carried out a detailed study of the Na_4^+ + Cs system at a lab collision energy of $E_{lab} = 2.7$ keV. The cluster projectile is prepared initially in its electronic and geometric (rhombic, D_{2h}) ground state. In Figure 1, the time evolution of the calculated average charge located on the Cs atom $\langle q_{Cs} \rangle(t)$ (obtained from a Mulliken population analysis) as well as of the kinetic-energy difference $\Delta E_{kin}(t) = E_{c.m.} - E_{kin}(t)$, where $E_{c.m.}$ and $E_{kin}(t)$ are the collision energy and the total kinetic energy, respectively, both referred to the center-of-mass frame, are presented for two collision events with the same impact parameter ($b = 9$ a.u.) but different initial orientations of the cluster with respect to the beam axis (see inserts (a) and (b) in Fig. 1). The quantity $\langle q_{Cs} \rangle(t)$ characterizes the quantum dynamics of CT, whereas $\Delta E_{kin}(t)$ describes the energy flow in the classical (ionic) degrees of freedom. A strong dependence of both quantities on the initial orientation of the cluster is observed. In the example (a), nearly compensating charge fluctuations during the interaction lead finally to $\langle q_{Cs} \rangle \approx 0$, and the event corresponds to a nearly elastic scattering $\Delta E_{kin} \approx 0$. In contrast, the large CT in the case (b) $\langle q_{Cs} \rangle \approx 0.75$ is accompanied by a considerable energy loss of $\Delta E_{kin} \approx 0.34$ eV. An endothermic character is typical for most collision events with appreciable CT, even at larger impact parameters, where no vibrational excitation of the cluster occurs. Comparing the ionization potentials of the Cs atom (3.89 eV) and the Na_4 cluster (4.24 eV [24]) and assuming a CT that results in the electronic ground state of Na_4, one should expect an exothermic reaction with $\Delta E_{kin} \approx -0.35$ eV. That this is not the case indicates that the CT process produces an electronically excited Na_4 cluster.

The calculation of CT cross-sections requires a detailed analysis of the final electronic and atomic states and, in particular, the careful consideration of CT probabilities for different reaction channels. To start with a transparent classification, we define integral CT probabilities, which are the probabilities $P(Cs^q)$ to find the Cs atom in the
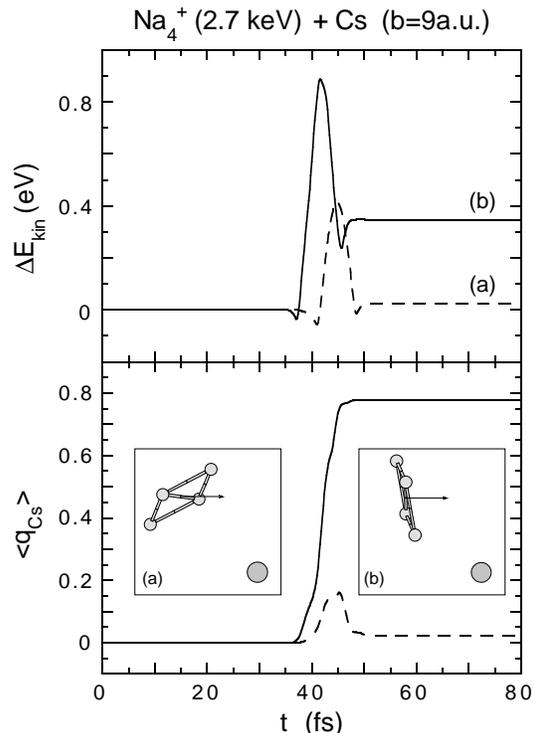

Fig. 1. Calculated kinetic-energy difference ΔE_{kin} (upper panel) and average value of the charge located on the Cs atom $\langle q_{Cs} \rangle$ (lower panel) as functions of time t for the two initial collision geometries illustrated in the inserts (a) and (b). The dashed and solid lines correspond to the cases (a) and (b), respectively.

charge state q in the exit channel, where q is an integer and $\sum_q P(Cs^q) = 1$. These probabilities describe the primary CT ($q \neq 0$) and scattering ($q = 0$) processes without regard to the further evolution of the cluster, i.e. to the possible fragmentation. The related CT cross-sections can be directly measured by detecting the formed Cs ions. The probabilities $P(Cs^q)$, calculated as an average of the results obtained with about 300 different initial orientations of the cluster per impact parameter b, are shown as a function of b in the upper panel of Figure 2. The CT leading to Cs^+ ions and the scattering without CT have nearly equal probabilities $P(Cs^+)$ and $P(Cs)$, respectively, for impact parameters $b \leq 8$ a.u. As the graph of $P(Cs^+)$ indicates, CT takes place with remarkable probability up to impact parameters of $b \approx 15$ a.u., which is more than twice the long half-axis ($R = 5.7$ a.u.) of the Na_4 rhombus. Surprisingly, the calculations also yield a finite probability $P(Cs^-)$ for an electron transfer to the Cs atom, which represents an interesting prediction for future experimental studies.

The b-weighted integration of $P(Cs^+)$ leads to a total CT cross-section of $\sigma(Cs^+) = (38.2 \pm 2.1)$ Å^2. For comparison, the "geometrical" cross-section of the cluster is about $\sigma_0 \approx \pi R^2 \approx 29$ Å^2 and the measured value is $\sigma^{exp}(Na_4) = (17 \pm 3)$ Å^2 [3]. It is important to realize, however, that, instead of Cs^+, the signal of the neutralized

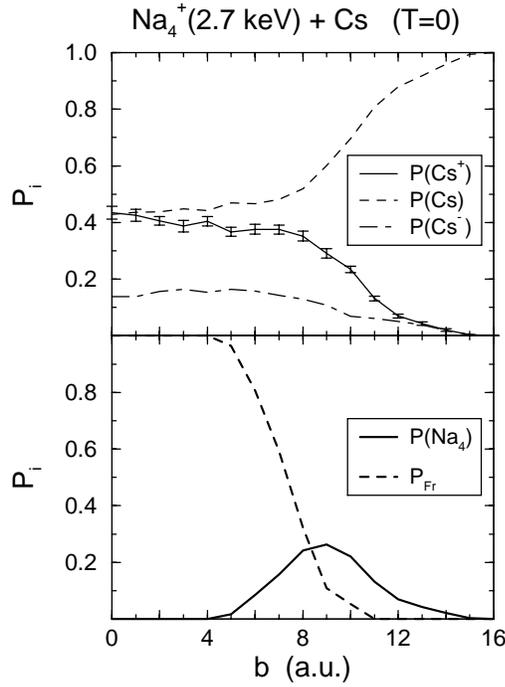## Na$_4^+$(2.7 keV) + Cs   (T=0)

Fig. 2. Calculated integral CT probabilities $P(\mathrm{Cs}^+)$, $P(\mathrm{Cs})$, $P(\mathrm{Cs}^-)$ (upper panel), and fragmentation P_{Fr} and CT probabilities $P(\mathrm{Na_4})$ (lower panel) as functions of the impact parameter b for Na$_4^+$ chosen initially at $T = 0$ K in its lowest-energy structure (see text). The length of the error bars is given by $2\,s_D$, where s_D is the standard deviation of the orientation average.

Na$_4$ was detected in the measurements [3]. The "survival" probability of the Na$_4$ cluster after the primary CT is given by $P(\mathrm{Cs}^+)$. $[1 - P_{Fr}]$, where P_{Fr} is the total fragmentation probability. In cluster collisions, fragmentation can be induced through three mechanisms characterized by different time scales [21,23,25]. These are large momentum transfer between atoms of the projectile and of the target, electronic excitation followed by energy transfer via electron-vibrational coupling, and statistical fragmentation. Whereas the first two mechanisms are precisely described by the NA-QMD theory and automatically accounted for in the actual calculations (this has been shown in comparisons with experimental data on CID [21]), the total probabilities of the different fragmentation channels can be determined from the calculated internal (vibrational and electronic) excitation energy of the cluster using statistical arguments [23]. The calculated total fragmentation probability P_{Fr} and the probability $P(\mathrm{Na_4})$ to have a neutral Na$_4$ cluster in the exit channel are shown as a function of b in the lower panel of Figure 2. Fragmentation occurs with high and then decreasing probability up to $b \approx 11$ a.u., and the computed total fragmentation cross-section of $\sigma_{Fr} = 49.4$ Å^2 exceeds the geometrical cross-section considerably. The CT probability $P(\mathrm{Na_4})$ peaks around $b \approx 9$ a.u., which is larger than the cluster "radius" R. The CT cross-section $\sigma(\mathrm{Na_4}) = 20.2$ Å^2 is still slightly larger than the experimental value.

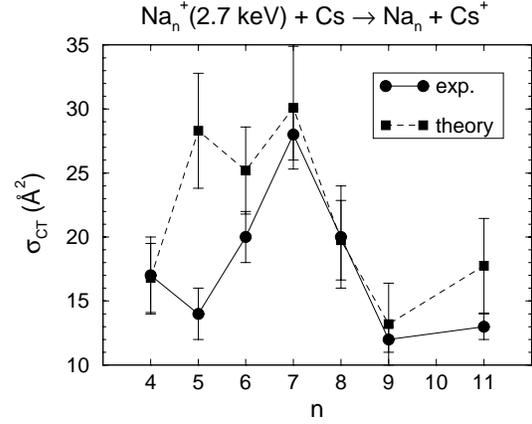## Na$_n^+$(2.7 keV) + Cs → Na$_n$ + Cs$^+$

Fig. 3. Calculated and measured [3] CT cross-sections $\sigma_{CT}(\mathrm{Na}_n)$. The theoretical error bars result from the statistical uncertainty $2\,s_D$ (*cf.* Fig. 2).

The calculations presented above have been performed at zero initial temperature of the cluster, whereas in the experiments [3,4] liquidlike cluster ions were used resulting from the laser ionization to produce the cluster beam [26]. To take into account the temperature effect, we have carried out simulations with excited clusters in the initial state (equilibrated over 300 ps). The calculated CT cross-section $\sigma(\mathrm{Na_4}) = 16.8$ Å^2 obtained with "liquid" cluster ions ($T \approx 700$ K [27]) is in perfect agreement with the experimental result. Within the temperature range for "liquid" but stable clusters 500 K $< T <$ 900 K the variation of $\sigma(\mathrm{Na_4})$ with T is smaller than the statistical uncertainty (2.7 Å^2).

The theoretical and experimental [3] CT cross-sections are compared as a function of the cluster size n in Figure 3. The theoretical results were obtained with "liquid" cluster ions in the initial state. Except for the case of $n = 5$, the agreement of the computed and measured data can be qualified as perfect, since these data are *absolute* cross-sections. The statistical uncertainties of the calculated cross-sections reflect the strong dependence of the outcome of the collision process on the initial configuration. These uncertainties could be reduced further only at a very high computational cost [23]. The overestimated cross section in the case $n = 5$ results from contributions of a particular isomer, for which accidentally a (quasi-)resonant CT with Cs occurs [23].

The distinct maximum of the experimental CT cross-section at $n = 7$ is reproduced by the calculations. This maximum, however, may be peculiar to the particular collision energy. In the experimental investigation of K$_n^+$ + Cs collisions [4] a very strong dependence of the CT cross-section on the collision energy has been found (*cf.* Fig. 4 in Ref. [4]). In order to examine this aspect and to stimulate further experimental investigations, we have calculated the CT cross-section over a wide range of the (center-of-mass) collision energy (0.1 ... 30 keV) for $n = 4, 7, 9$. The results are shown in Figure 4. The absolute CT cross-section for $n = 7$ exceeds those for $n = 4$ and $n = 9$ over the entire energy range considered. Consequently,
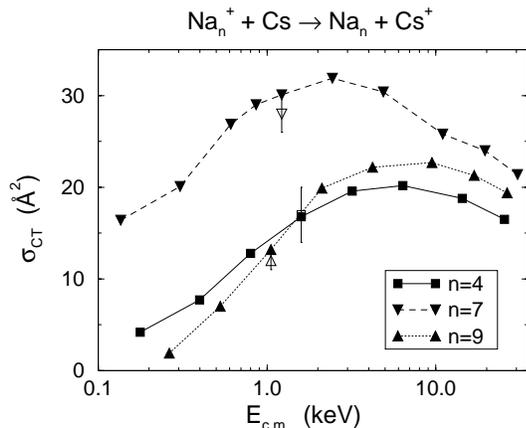
$$Na_n^+ + Cs \rightarrow Na_n + Cs^+$$

Fig. 4. Calculated collision energy dependence of the CT cross-section $\sigma_{CT}(Na_n)$ for $n = 4, 7, 9$ (full symbols). The experimental data (open symbols with error bars; [3]) correspond to the same lab collision energy of $E_{lab} = 2.7$ keV.

the large CT cross-section in Na_7^+ + Cs collisions should be attributed to the specific electronic structure of Na_7^+ providing favorable, *i.e.* near resonant conditions for CT in collisions with Cs.

In summary, we have presented results of a fully microscopic analysis of CT and fragmentation in cluster-ion – atom collisions based on NA-QMD simulations. The detailed study of $Na_4^+(2.7$ keV$)$ + Cs collisions revealed the role of the different physical processes associated with CT in cluster collisions (electronic excitations, fragmentation, temperature effects). An exotic "inverse" CT process leading to Cs^- is predicted. The calculated absolute CT cross-sections for $Na_n^+(2.7$ keV$)$ + Cs $(4 \leq n \leq 11)$ are in good agreement with the experimental data. The energy dependence of the CT cross-section is predicted for several cluster sizes $(n = 4, 7, 9)$ in order to encourage further experimental studies.

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