# Direct Observation of Charge-Exchange Collisions between Mass-Selected $Na_n{}^+$ Clusters and Cs Atoms

C. Bréchignac, Ph. Cahuzac, J. Leygnier, R. Pflaum,[(a)] and J. Weiner[(b)]
*Laboratoire Aimé Cotton, 91405 Orsay Cédex, France*
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We have measured total charge-exchange cross sections in collisions between mass-selected $Na_n{}^+$ cluster ions ($1 \leq n \leq 21$) and atomic cesium. Cross sections for clusters ranging from the monomer to the 21-mer lie between 40 and 10 Å$^2$, decreasing slowly with increasing mass. Fast neutral products of charge exchange are photoionized and mass analyzed in a secondary time-of-flight spectrometer. Charge-transfer products present a narrow distribution of at most three masses $Na_n$, $Na_{n-1}$, and $Na_{n-2}$, with the most probable product being $Na_n$ or $Na_{n-1}$.

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The fundamental motivation for the study of clusters is to understand how atomic and molecular properties transform to those of the solid state as the size of the aggregate increases. It is not surprising therefore that the recent past has seen a flurry of activity in the investigation of mass-selected cluster ions[1] since electronic properties, stabilities, and reactivity can be determined as functions of incremental mass. Until now, however, very few experiments have come to grips with the difficult but important problem of mass-selected *neutral* clusters. Early work on charge-exchange neutralization in hydrogen,[2] silicon,[3] and sulfur[4] clusters suffered from a lack of direct information on the mass distribution of post-charge-exchange neutrals, therefore leaving open the question of possible product dissociation.

We report here a study of charge exchange between mass-selected sodium cluster ions $Na_n{}^+$ and Cs atoms,

$$Na_n{}^+ + Cs \rightarrow Na_n + Cs^+, \quad 1 \leq n \leq 21. \tag{1}$$

We measure the cross section for process (1) to lie between 40 and 10 Å$^2$ and to decline slowly with cluster size. Post-collision photoionization of the charge-exchanged neutral products permits for the first time a direct measure of the final mass spectrum. The reionization spectrum associated with process (1) presents a simple pattern with the principal peak falling on the parent or on the $(n-1)$-mer.

The experimental apparatus is shown in Fig. 1. An unseeded adiabatic expansion through a 0.1-mm-diam conical nozzle produces neutral sodium clusters[5] which are then ionized by a nitrogen laser focused between the first two plates of an ion-focusing and -acceleration system. The plate voltage determines the ion beam energy and can be set between 1 and 3 keV. After acceleration and focusing, the ions enter a drift region where they spatially resolve into individual mass packets. The ion packets pass between two electric-field plates which deflect all charged particles from the beam path. When the packet of interest arrives at the deflection plates, the field momentarily pulses off to allow the selected packet to proceed down the beam path undeflected. The cluster group then enters a 15-cm-long alkali-metal heat pipe[6] where a uniform atomic density can be maintained at pressures low enough to insure single-collision conditions. Two diaphragms downstream from the alkali-metal cell limit the observed scattering angle to 10 mrad in the forward direction, and thus discriminate against large-scattering-angle collisional events. After passage through the angle-limiting diaphragms, residual ions and product neutrals enter a second acceleration region. There we choose either to redisperse and measure the fragmentation of the surviving ion clusters or to reionize the product neutrals with a second uv laser pulse before subjecting them to the second acceleration field. A final field-free region again spatially disperses the product-ion packets which are at last detected by a high-gain particle multiplier mounted at the end of the beam line. A typical spectrum for $Na_9{}^+$ (after redispersion but without reionization) is shown in Fig. 2. Peaks correspond to (a) surviving parent ion, (b) fragment ions arising from collision-induced dissociation, and (c) fast neutrals arising principally from the charge-transfer process discussed in detail below.

In order to analyze the component masses of the neu-

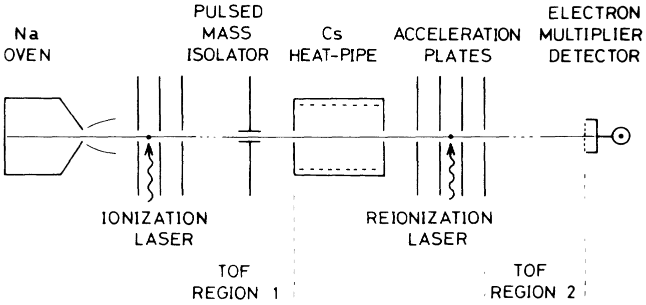

FIG. 1. Schematic diagram showing the essential elements of the apparatus. The first two acceleration plates serve as the angle-limiting apertures.

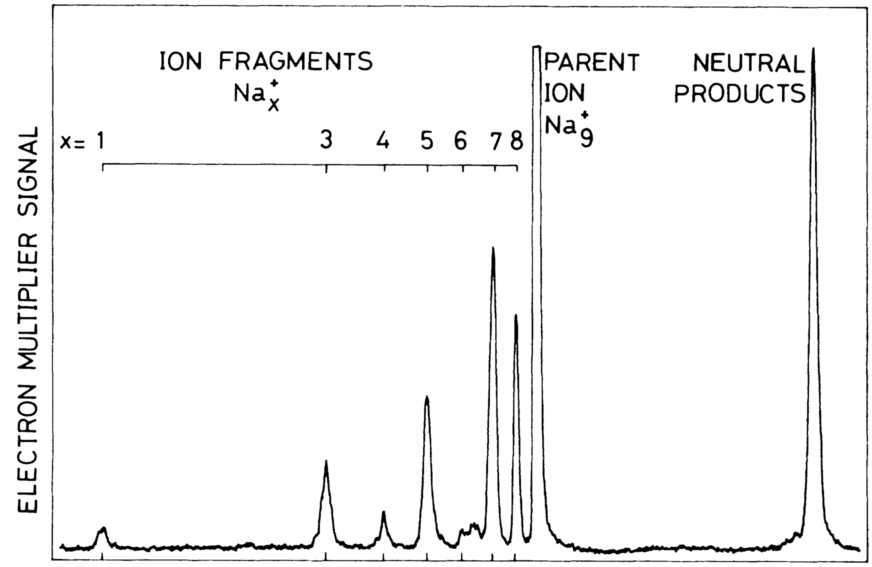

FIG. 2. Typical mass spectrum of $Na_9{}^+$ showing the essential features of the collision and dissociation processes. Note that the neutral-product peak is detected *without* reionization and the fragment ions are dispersed in the acceleration region after the heat pipe (see Fig. 1).

tral packet, we first sweep away the incident ions and reionize the neutrals with the second pulsed uv laser. The reionization spectra for any cluster is a function of not only the collision process from which it arises but also the photon energy and flux of the reionization laser pulse. We judiciously choose the photon energy to lie above the ionization limit[7] but below the dissociation energy[8,9] of the relevant species. In addition, we attenuate the laser power density so as to carry out measurements only in a regime in which the relative peak heights of the reionization spectra are independent of photon flux and the intensity is linear with photon flux. Under these conditions the reionization mass spectrum produces a direct measure of the fast-neutral mass pattern. In all cases, the spectra present a very narrow distribution of at most three masses, with the principal peak falling on either $Na_n$ or $Na_{n-1}$. Figure 3 shows a series of reonization spectra for $Na_3$, $Na_7$, and $Na_9$. The spectra of $Na_3$ and $Na_7$ show mostly the parent, evidently due to charge exchange. In contrast, for $Na_9$ the reionization spectrum shows $Na_8{}^+$ dominating the mass spectrum, indicating that an evaporation of a monomer is associated with the charge transfer. Higher masses (e.g., $Na_{21}$) also exhibit evaporation of a single atom in the reionization spectrum.

In addition to charge transfer, fast neutrals may also arise from collisional dissociation,

$$Na_n{}^+ + Cs \rightarrow Na_{n-p}{}^+ + Na_p + Cs. \qquad (2)$$

Indeed, Fig. 2 indicates extensive fragmentation of the detected *ion* spectrum arising from process (2), and if the corresponding neutral partners were the sole contributors to the neutral spectrum they would also exhibit a wide fragmentation pattern. The neutral spectrum *actually observed* shows very little fragmentation and thus cannot arise from ion collisional dissociation. The contribution to the neutral spectrum intensity from fragmentation is negligible for two reasons: First, collisional dissociation occurs principally by evaporation of monomers or dimers and kinematics dictates that the light particles be ejected off the beam axis away from the detector acceptance angle. Second, the reionizing uv photon has insufficient energy to ionize the monomer and dimer in a single step. Then the photoionization efficiency of these two species is greatly reduced. Supporting evidence comes from a separate experiment[10] in which we observed the evaporation of aggregates in collisional dissociation in $K_n{}^+$ + Na collisions.

The reionization step can be used not only to detect the result of the collisional process but also to probe the internal states of the neutralized products. Preliminary photoionization spectra, measured at several different wavelengths,[11] reveal internal excitation of the charge-transfer products. In certain cases the internal modes are sufficiently "hot" to permit monomer (or dimer) evaporation as observed for $Na_9$ and $Na_{21}$. In the latter two cases the tendency to evaporate an atom is probably due to the relative stability of the closed electron shells in $Na_8$ and $Na_{20}$.

The quasiresonance of process (1) for $Na_n{}^+$ ($n \geq 3$) results in a strong neutralization signal (15% of the reactant-ion beam packet intensity). The secondary neutrals formed by charge exchange have essentially the same velocity and the same trajectory as the incident ion

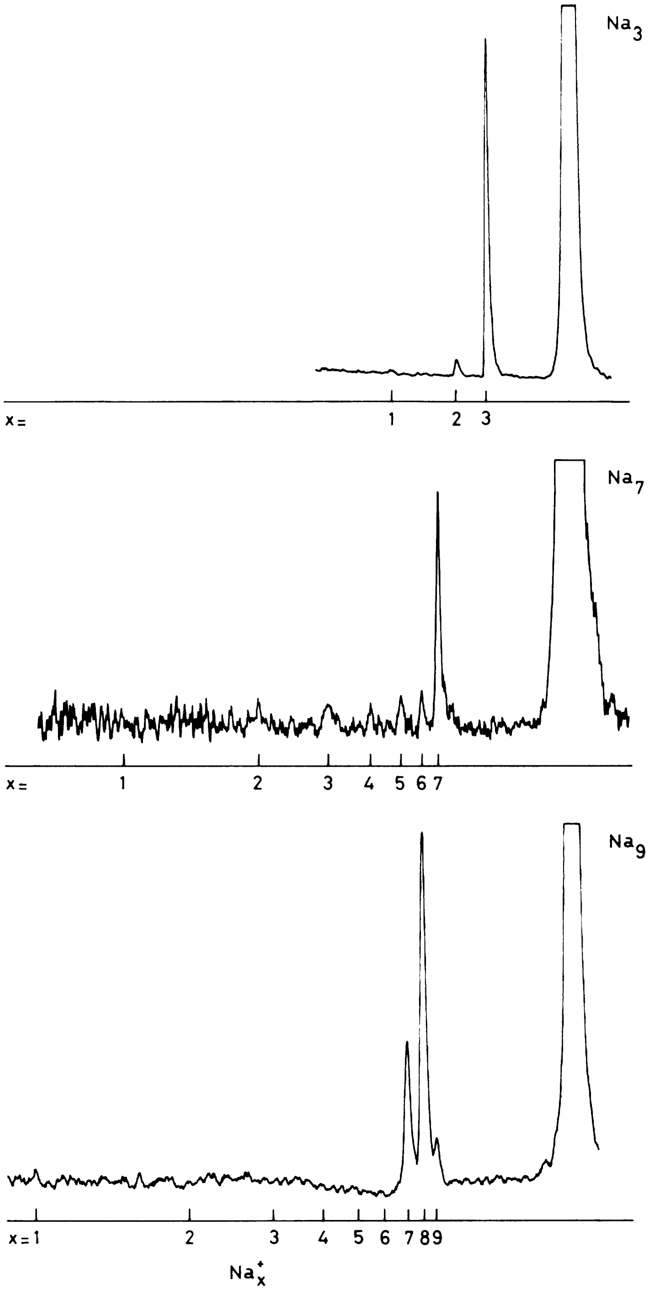

FIG. 3. Three reionization mass spectra of the neutral charge-transfer products from (top to bottom) $Na_3{}^+$, $Na_7{}^+$, and $Na_9{}^+$ parent ions. The large peaks on the right-hand side correspond to the neutral products and the sharp peaks correspond to the narrow distribution of the ionized neutrals.

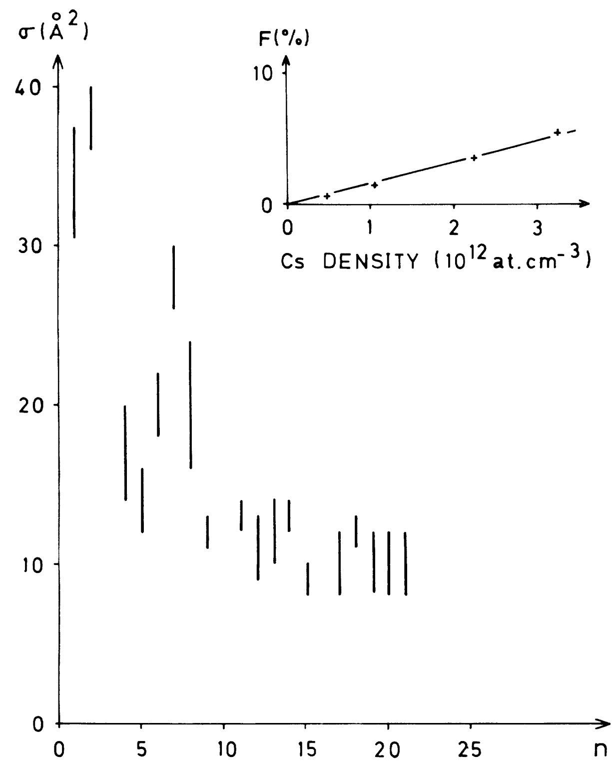

FIG. 4. Charge-exchange cross section vs cluster size for $Na_n$ $(1 \leq n \leq 21)$. Inset: The fraction $F$ of $Na_9{}^+$ aggregates neutralized vs Cs density. The slope of the linear plot is proportional to the charge-exchange cross section. Plots similar to the inset were developed for each cluster.

species, and thus the collisional process involves little momentum transfer. These results are consistent with those obtained by translational spectroscopy of molecules[12] and recently for $S_n$ $(n \leq 8)$.[4] Moreover, the narrow neutral distribution shows that at most one atom or one dimer is evaporated after the charge-exchange collision. Since the atomization energies of small sodium clusters are about 0.7 eV,[8,9] the energy transferred to the neutral during the charge-exchange collision must be about the same, consistent with a weakly interacting, long-range process.

The charge-exchange cross sections are determined in a Beer's-law experiment by the measurement of the ratio of neutral intensities to incident $Na_n{}^+$ $(1 \leq n \leq 21)$ as a function of Cs density. Figure 4 summarizes the results. The measured charge-transfer cross section (40 Å$^2$) for $Na^+ + Cs$ is in good agreement with previous results obtained by Marino under similar experimental conditions.[13] The rather slow decline of the charge-transfer cross section as a function of aggregate size differs markedly from the collisional-dissociation channel observed in the $K_n{}^+ + Na$ system which exhibits a marked odd-even alternation of fragment intensities and increases roughly with $n$ (Ref. 10). The cross-section magnitude and cluster-size behavior of process (1) is consistent with the familiar Landau-Zener-Stückelberg formulation of charge transfer[14] in which maximum probability for the electron jump is localized to a small region of far intermolecular separation ($\simeq 11$ Å). The conventional picture of charge transfer envisions the crossing (or near crossing) of two well-defined adiabatic electronic states at the point of maximum probability. The final state of the transferred electrons need not be exclusively the ground state of the neutralized aggregate, and the evaporation of an atom or dimer in process (1) indicates that the initial transfer may be in some cases to an excited electronic state, which subsequently decays via vibronic coupling. These adiabatic states correspond to single-particle excitations, distinct from electron collective oscillation at the surface plasma frequency. Although single-particle excitations have been predicted in the optical spectrum of sodium clusters,[15] their existence has not yet been confirmed by experiment;[16] and the extent to which they may be damped by strong vibronic coupling remains an open question. The behavior of process (1) as well as the cluster optical absorption spectrum must be consistent with a physical picture which takes into proper account the relative importance of single-particle and collective modes of excitation. The elucidation of aggregate excited states is therefore of prime importance for the understanding of cluster collision dynamics.

In summary, we have measured the charge-transfer cross section of mass-selected sodium-ion clusters and have shown that the resulting neutral products either conserve the parent mass or evaporate at most either one atom or dimer. The reionization mass spectrum of $Na_9$ shows evidence of internal excitation. The neutralization process not only is useful for the investigation of the physics of cluster collision dynamics, but also provides a size-selected source of neutral aggregates for further experiments.

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[a] Permanent address: Fakultät für Physik, Universität Konstanz, Bücklestrasse 13, Postfach 5560, D-7750 Konstanz 1, Federal Republic of Germany.

[b] Permanent address: Department of Chemistry, University of Maryland, College Park, MD 20742.

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