

Initial-state control in mutual neutralization of Si^- with Na^+ or K^+ revealing strong violations of Wigner's spin-conservation rule

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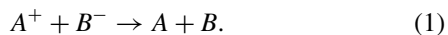
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We have studied low-energy mutual neutralization in reactions of Si^- with Na^+ and with K^+ ions at the merged-beam double ion-beam storage-ring facility DESIREE. We made measurements with and without a significant fraction of the Si^- ions in the metastable ^2D level. The latter was achieved by state-selective photodetachment. The data reveal contributions from spin-forbidden mutual-neutralization reactions, i.e., violations of Wigner's spin-conservation rule. For the $\text{Na}^+ + \text{Si}^-$ case, the dominating such reaction channel is obscured when metastable Si^- ions are present in the beam.

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I. INTRODUCTION

In the fundamental collision process of mutual neutralization (MN), charge is exchanged between two initially singly charged ions, one anion and one cation, to form two or more neutral particles. In the general case of two molecular ions, this can lead to different product-mass distributions [1], but in the fundamental case of two singly charged atomic ions considered here, the MN products are always two neutral atoms A and B :



Despite the apparent simplicity of the process, an advanced theoretical analysis is required in order to predict the total and angular-differential cross sections for this process, as well as the final quantum-state distributions of the neutral atoms formed [2–6]. Measurements of MN with final-state selectivity in merged-beam setups have been performed earlier in a single-pass experiment [7] and at the merged-beam storage-ring facility used in the present work [8–13].

While those previous experiments demonstrated the ability to determine the final states of the formed neutral atoms, the present work is focused on the control of the initial states of the interacting ions. Contributions from excited states with lifetimes up to the range of seconds or even a few minutes can

be removed by storing the ions for longer than that. However, in many cases the lifetime of long-lived metastable states may exceed the ion-beam storage lifetime [14]. When the anion is the collision partner with a long-lived excited state, the ions' internal state distribution can be manipulated by state-selective photodetachment techniques [15,16].

In this work we present results on MN where the initial quantum-state distribution was actively manipulated by depleting the population in the metastable ^2D state of Si^- via laser photodetachment. This way, we measured MN with a pure ground state $\text{Si}^-(^4S)$ beam interacting with ground-state beams of either Na^+ or K^+ (see Fig. 1 for unperturbed state energies in Si^- , Na , and K). By this procedure, we reveal contributions relating to excitation of the resulting Si atom, which in the data sets recorded without the laser depletion are obscured by contributions from reactions with anions in the metastable $\text{Si}^-(^2D)$ state. In most collision processes, the total electronic spin is conserved, in accordance with Wigner's spin-conservation rule [17,18], and therefore non-spin-conserving channels are generally neglected in mutual-neutralization calculations [2–6]. However, as will be discussed below, our measurements reveal clear evidence of reactions that proceed despite violating this rule.

II. EXPERIMENTAL SETUP AND PROCEDURES

A. Mutual-neutralization measurements

The experiments were performed at the double electrostatic ion-ring experiment (DESIREE) facility at Stockholm University, Sweden [19,20]. DESIREE features a dual electrostatic ion-beam storage ring uniquely designed to operate in an ultrahigh-vacuum environment and at a cryogenic temperature (approximately equal to 13 K). This setup provides an ideal

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platform for achieving precise control over ion interactions in the merging region enabling final-state resolved studies of MN processes with stored ions. In this work we manipulated the initial quantum states of the stored ions before the MN reactions. A schematic of the experimental setup is shown in Fig. 2.

Two beams of singly charged ions, one positive and one negative, were mass selected by bending magnets and guided into the storage rings, where they overlapped in the merging region as shown in Fig. 2. There, a series of seven drift tubes, with a total length of 56 cm, was used to fine-tune the ion-beam velocities to achieve a low center-of-mass collision energy by biasing one or a few of the tubes at a suitable voltage. At the end of the merging section, electrostatic deflectors bent the ion beams into their closed orbits, while the neutral products continued along straight-line trajectories to the imaging detector (ID). The ID consists of three stacked 75-mm-diam low-resistance microchannel plates, followed by a phosphor-screen anode and a Tpx3Cam camera [21] viewing the phosphor screen from outside the vacuum system through a window. The Tpx3Cam, equipped with a 256×256 pixel array and a photon-counting sensor, allows multihit coincidence detection. This setup simultaneously measures the arrival time and position of the particles, thereby determining the three-dimensional vector displacement $\vec{r}$ of the two neutral reaction products as their center of mass crosses the detector plane.

The magnitude of this vector is the product separation r and is determined by the sum of the kinetic energies of the two neutral particles in their center-of-mass frame, which through energy conservation is given by $E_{k,f} = E_{k,i} + \Delta E_k$. Here indices i and f indicate initial and final values of the total center-of-mass kinetic energy, respectively, and ΔE_k is the kinetic energy released in the reaction, which is equal to the decrease in total electronic energy associated with the given initial and final states. In the analysis, the experimental $E_{k,f}$ values are deduced from the measured values of r through

$$E_{k,f} = \frac{\mu}{2} \left(\frac{rV}{L} \right)^2, \quad (2)$$

where V is the velocity of the center of mass in the laboratory, μ is the reduced mass, and L is the distance between the position of the collision and the detector. In the experiment, a part of the merged-beam section is put on a bias voltage to reach a low value of $E_{k,i}$. Collisions resulting in MN, but taking place outside of the biased region, will have much larger values of $E_{k,i}$ (and thus of $E_{k,f}$ and r) and are easily separated from the events of interest with low $E_{k,i}$. The length of the biased region is important as it determines the uncertainty of the flight distance L . For the highest resolution, a short biased section was chosen, while a longer section has the advantage to yield a higher signal rate.

Two collision systems are considered in the present work: $\text{Na}^+ + \text{Si}^-$ and $\text{K}^+ + \text{Si}^-$. In the former case, $^{23}\text{Na}^+$ ions were produced using an electron cyclotron resonance ion source with heated NaBr powder. The ions were then accelerated to 9.08 keV and stored in the asymmetric ring (see Fig. 2). Simultaneously, $^{28}\text{Si}^-$ ions were produced from a solid silicon rod using a cesium sputtering source, accelerated

to 10.0 keV, and stored in the symmetric ring. For the $\text{Na}^+ + \text{Si}^-$ experiment, three drift tubes with a combined length of 23.3 cm were biased at +474 V, giving an average flight distance from collision to detection of $L = 176.49$ cm. In the $\text{K}^+ + \text{Si}^-$ experiment, the beam energies were set to 14.0 keV for $^{39}\text{K}^+$ and 9.0 keV for $^{28}\text{Si}^-$ and with a bias of +613 V on a single drift tube of length 6.60 cm at a distance of $L = 192.37$ cm from the imaging detector.

Different parameters are chosen in the two experiments. In the case of $\text{Na}^+ + \text{Si}^-$, the main focus was to establish a clearly visible difference in the MN data depending on the metastable fraction of the Si^- beam, while for the case of $\text{K}^+ + \text{Si}^-$, we aimed for the highest possible resolution in order to detect small contributions from additional MN final-state channels.

B. Laser photodetachment of metastable Si^- ions

As shown in Fig. 1, the electron affinity of silicon is 1.39 eV, and the Si^- anion ground-state term is ^4S . In addition, two long-lived excited states exist: ^2D , which is bound by 0.53 eV, and ^2P , which is very loosely bound by 0.03 eV. Both the ^2D and ^2P terms are fine-structure doublets, but with splittings of only a few meV [22] such that the fine structure is not resolved in the present study. In a study of Si^- at the cryogenic storage ring [23], the ion beam was produced using a sputter ion source similar to that employed in the present experiment, where a population of about 3% in the ^2D state and much less in the ^2P state was found. For ^2D , a lower limit to the lifetime of 5.7 h was established by Müll *et al.* [22], while they measured the ^2P lifetime to be 22.2 ± 2.5 s [22]. For MN studies, we thus anticipate a small but measurable contribution from anions occupying the ^2D term, even when the ions are stored for several tens of seconds or longer.

A laser photodetachment signal was recorded using 900-nm, 5-ns pulses from a 1-kHz optical parametric oscillator (OPO) in a crossed-beam configuration as shown in Fig. 2. Neutral silicon atoms produced by photodetachment were detected on the ID at the end of the merging region. At this wavelength, the photon energy is 1.38 eV, and photodetachment only occurs for anions in the metastable level. The detected rate of neutrals from photodetachment is thus proportional to the number of stored ions, which occupy the metastable level. The metastable population was reduced to essentially zero by applying a continuous-wave (cw) laser (also at 900 nm) along the injection straight section of the symmetric ring (see Fig. 2), while the pulsed laser in the merging section simultaneously recorded the resulting neutrals. This procedure effectively eliminated the metastable component within tens of seconds, and the measured signal is shown in Fig. 3 as a function of time after injection. The red curve shows data recorded in a 10- μs -wide gate around the time of arrival of neutral Si atoms produced in photodetachment by the OPO laser with the cw laser on during the whole measuring cycle. The blue curve shows data recorded in a 100- μs -wide gate recorded between laser pulses and divided by 10 for direct comparison. The initial much higher counts around the OPO pulses is due to photodetachment of metastable Si^- ions, and the fact that the red and blue curves coincide after tens of seconds shows that very few

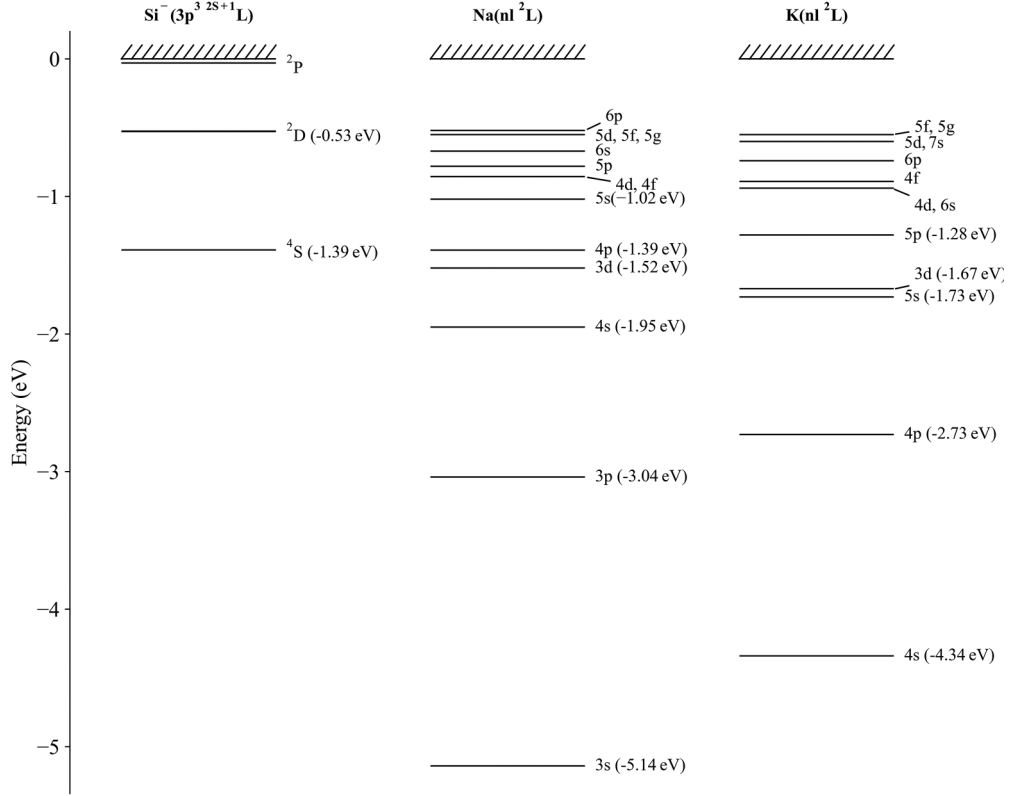


FIG. 1. Energy-level diagrams of the negative silicon ion and neutral sodium and potassium atoms, where states up to $6p$ and $5g$ are presented for Na and K, respectively. For Na and K, the total angular momentum L is given by the angular momentum l of the outermost electron $L = l$. Horizontal lines indicate the bound electronic states, while slanted lines at zero energy represent the continuum of the active electron. The energies indicated correspond to the levels considered in Tables I and II.

metastable ions are left to photodetach, and the signals are likely dominated by neutrals formed in residual-gas collisions at this point. Thus, after tens of seconds of storage with the cw laser on as shown in Fig. 2, we have a circulating Si^- beam with essentially all ions in the ground state $4S$. After 60 s, the beam is dumped and only detector dark counts are left. Figure 3 demonstrates our ability to control whether beams of Si^- ions have a significant metastable component or not. We make use of this control in the MN experiments, the results of which are discussed below.

III. LANDAU-ZENER MODEL CALCULATIONS

Mutual neutralization can be modeled using semiclassical Landau-Zener calculations. The potential-energy curves associated with the ion-pair limits of Na^+ or K^+ and Si^- will give rise to molecular states governed by an attractive Coulomb potential at large internuclear distances. In a diabatic representation, where the characters of the states are preserved, the potentials of the ion pair will cross potentials that dissociate into the channels of neutral atomic fragments. If the molecular states of the crossing potentials then have the same symmetry, they will couple by electronic couplings ($H_{ij} = \langle i | \hat{H}^{\text{el}} | j \rangle$). In the Landau-Zener model [24,25], the probability for following the states diabatically through the curve crossing is given by

$$p_{ij} = \exp\left(-\frac{2\pi H_{ij}^2}{v_r \left|\frac{d}{dR}(V_i - V_j)\right|}\right). \quad (3)$$

Here the electronic coupling H_{ij} , the difference of slopes of the two crossing diabatic potentials $\frac{d}{dR}(V_i - V_j)$, and the radial velocity v_r are all evaluated at the curve-crossing distance. The ion-pair states will cross several of the potential-energy curves associated with neutral atoms in different electronic states. The final-state distribution is computed by adding probabilities for neutralization from all possible pathways as described in [26].

Since the electron transfer occurs at large internuclear distances, the potential-energy curves are approximated with

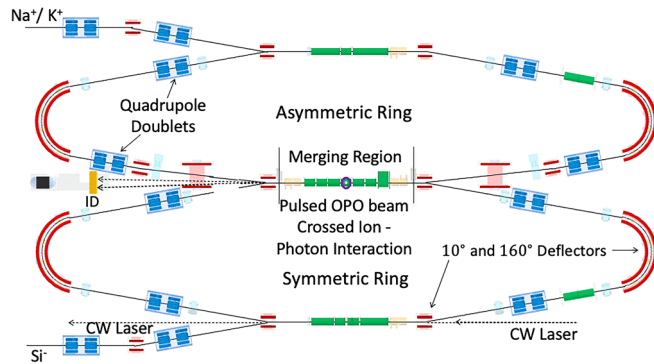


FIG. 2. Schematic of the DESIREE facility, highlighting the double electrostatic storage-ring configuration and its components for stored ion-beam interaction studies at cryogenic conditions.

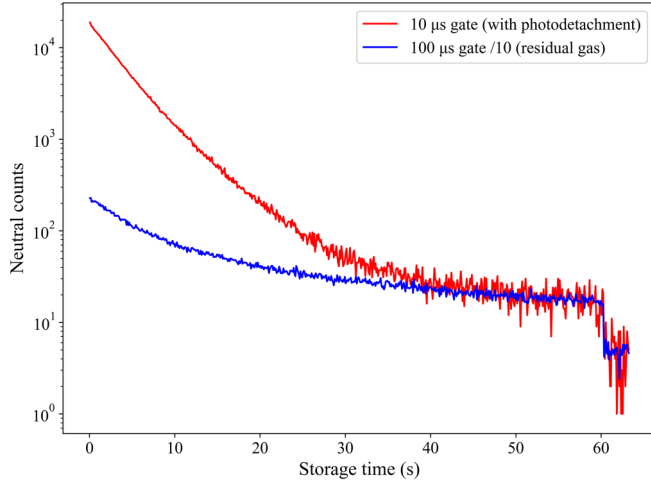


FIG. 3. Depletion of metastable Si^- ions as a function of storage time. The red curve shows the 10- μs -long gated neutral yield including the neutral particles from the laser photodetached metastable ions. The blue curve shows the neutral yield from residual gas and excluding the contributions from the laser photodetachment data recorded in a 100- μs -wide gate recorded between laser pulses and divided by 10 for direct comparison. After 50 s of storage the two curves coincide, which shows that both signals are dominated by neutralization in collisions with the neutral gas while any contribution from photodetachment of metastable Si^- then is insignificant in the red curve.

their asymptotic forms. In the present model calculations, the potentials of the ion-pair states are assumed to be of the form (in a.u.) $V_{ip}(R) = -\frac{1}{R} - \frac{\alpha_1 + \alpha_2}{2R^4}$, where α_i are the polarizabilities of the colliding ions [27]. The contribution from the last term, which contains the polarizabilities of the ion-pair potential, has only a minor influence on the calculated cross sections and branching ratios. The polarizability of the metastable (^2D) state of Si^- is assumed to be identical to that of the ground state. We have verified that even increasing the metastable-state polarizability by an order of magnitude does not produce any significant change in the calculated branching ratios. The potentials of the covalent states are approximated as constant. Ionic-covalent electronic couplings between states of the same Λ - S symmetry are considered. In

the case of collisions between $\text{Na}^+(^1S)$ or $\text{K}^+(^1S)$ and $\text{Si}^-(^4S)$, molecular states of $^4\Sigma^-$ symmetry are considered. For collision of $\text{Na}^+(^1S)$ or $\text{K}^+(^1S)$ with the metastable $\text{Si}^-(^2D)$, molecular states of $^2\Sigma^-$, $^2\Pi$, and $^2\Delta$ symmetries are formed. The statistical ratios due to the degeneracies of the molecular states have to be considered when the final-state distribution is computed.

The electronic couplings H_{ij} are calculated using two different approaches. First we used an anion-centered asymptotic model (ACAM) [4], i.e., a linear-combination-of-atomic-orbitals type approach, in which only one active electron shell for the neutralized atom and one active shell for the anion are considered. We used the Landau-Herring [28] method or Firsov integral [29]: a spherical integral of the Wronskian [30] of the ionic and covalent asymptotic wave function on a sphere centered on the anion. For proper normalization of the anion wave function, an asymptotic factor of 1.17 was introduced [31,32], and the anion polarizability was obtained from [27]. The electronic couplings, initially computed in an atomic basis, are transformed into the molecular-state basis under the assumption of Russell-Saunders (LS) coupling for the atomic states. In the alternative approach, we applied a semiempirical method developed by Olson [33]. In this approach, the coupling elements are estimated based on the curve-crossing distances, electron affinities, and effective ionization energies of the neutralized cation. The Landau-Zener calculations are performed at the collision energies in the present experiments. The results of both approaches are listed in Tables I and II for MN with $\text{Na}^+ + \text{Si}^-$ and for MN with $\text{K}^+ + \text{Si}^-$, respectively. Data on calculated crossing distances, coupling strengths, mutual-neutralization cross sections, and final-state distributions are provided in the data repository [34].

IV. RESULTS

A. MN with $\text{Na}^+ + \text{Si}^-$

In Fig. 4 we show the measured yield of neutral pairs as a function of the total kinetic energy $E_{k,f}$ associated with the MN process for Na^+ with Si^- , where the $E_{k,f}$ values are deduced from the measured product separations r using Eq. (2) and displayed for the range $0.3 \text{ eV} \leq E_{k,f} \leq 4.0 \text{ eV}$ where the detector system can reliably determine this quantity. The

TABLE I. Kinetic-energy releases ΔE_k and calculated cross sections and branching fractions for mutual neutralization between Na^+ and Si^- . Cross sections and branching fractions are calculated using couplings from the ACAM or using semiempirical couplings from Ref. [4,33].

Initial channel		Final channel		ΔE_k (eV)	Cross section (cm^2)		Branching fraction (%)	
Na^+	Si^-	Na	Si		ACAM[4]	Olson [33]	ACAM[4]	Olson [33]
^1S	^4S	$3s^2S$	$3p^2^3P$	3.75	0	1.058×10^{-17}	0	4.895×10^{-2}
^1S	^4S	$3s^2S$	$3p^2^1D$	2.969				
^1S	^4S	$3s^2S$	$3p^2^1S$	1.841				
^1S	^4S	$3p^2P$	$3p^2^3P$	1.647	2.078×10^{-14}	2.161×10^{-14}	99.95	99.95
^1S	^4S	$3p^2P$	$3p^2^1D$	0.866				
^1S	^4S	$4s^2S$	$3p^2^3P$	0.559	1.065×10^{-17}	1.269×10^{-25}	0.05	5.871×10^{-10}
^1S	^2D	$3d^2D$	$3p^2^3P$	0.992	5.227×10^{-14}	1.850×10^{-13}	19.03	46.94
^1S	^2D	$4p^2P$	$3p^2^3P$	0.862	1.501×10^{-13}	2.062×10^{-13}	54.65	52.36
^1S	^2D	$5s^2S$	$3p^2^3P$	0.492	7.229×10^{-14}	8.736×10^{-16}	26.32	0.221

TABLE II. Kinetic-energy releases ΔE_k and calculated cross sections and branching fractions for mutual neutralization between K^+ and Si^- . Cross sections and branching fractions are calculated using couplings from the ACAM or using semiempirical couplings from Ref. [4,33].

Initial channel		Final channel		ΔE_k (eV)	Cross section (cm ²)		Branching fraction (%)	
K^+	Si^-	K	Si		ACAM[4]	Olson [33]	ACAM[4]	Olson [33]
$1S$	$4S$	$4s^2S$	$3p^2^3P$	2.951	0	3.967×10^{-23}	0	7.211×10^{-9}
$1S$	$4S$	$4s^2S$	$3p^2^1D$	2.171				
$1S$	$4S$	$4p^2P$	$3p^2^3P$	1.341	5.9801×10^{-13}	5.502×10^{-13}	100	100
$1S$	$4S$	$4s^2S$	$3p^2^1S$	1.043				
$1S$	$4S$	$4p^2P$	$3p^2^1D$	0.561				
$1S$	$4S$	$5s^2S$	$3p^2^3P$	0.344	8.8462×10^{-24}	0	0	0
$1S$	$2D$	$3d^2D$	$3p^2^3P$	1.143	2.9097×10^{-13}	2.591×10^{-13}	27.42	33.28
$1S$	$2D$	$5p^2P$	$3p^2^3P$	0.753	7.4717×10^{-13}	5.044×10^{-13}	70.40	64.80

data in red are recorded after the metastable component of the Si^- beam was depleted by photodetachment by the cw laser (see Fig. 2) for 60 seconds, while the blue data are recorded without any laser depletion. The data are normalized such that the area of the dominating peak is the same for the two data sets.

Since the experimental data in Fig. 4 give the total kinetic energy $E_{k,f}$ rather than the kinetic-energy-release values ΔE_k directly, we anticipate a shift by the average initial collision energy value $E_{k,i}$. The dominating peak in Fig. 4 stretches from around 1.5 eV to 2.2 eV with a centroid value of (1.781 ± 0.020) eV, where the dominating source of error is an estimated 1-cm uncertainty of the average value of L due to a possible small change in transverse overlap along the direction of the beams [8]. The width and position of this peak are consistent with the reaction channel $Na^+(1S) + Si^-(4S) \rightarrow Na(3p^2P) + Si(^3P)$ at 1.647 eV and an average initial kinetic energy $E_{k,i}$ of (0.134 ± 0.020) eV.

To connect these experimental observations with the theoretical picture, Fig. 5 compares the diabatic potential-energy

curves with the kinetic-energy release ΔE_k spectra for the MN process between Na^+ and Si^- . The ΔE_k spectrum shown here was obtained subtracting an initial kinetic energy of (0.134 ± 0.020) eV from the measured $E_{k,f}$ values (see Fig. 4). To better visualize the weaker channels, the spectral intensities are presented on a logarithmic scale. Horizontal lines have been added in Fig. 5 to indicate the ΔE_k for different reaction channels as indicated to the far right in Fig. 5.

As the main peak is due to a reaction involving ground-state Si^- ions, it is unaffected by the 900-nm photodetachment lasers. For the smaller peak around 1.0 eV, however, there is a strong reduction when the metastable component is eliminated from the beam, although a clearly significant signal remains. We ascribe a strong contribution from metastable $Si^-(^2D)$ ions due to the reaction $Na^+(1S) + Si^-(^2D) \rightarrow Na(4p^2P) + Si(^3P)$. The experimental data are consistent with this channel being the only contribution with a metastable $Si^-(^2D)$ initial anion state. However, we cannot exclude a contribution from the reaction $Na^+(1S) + Si^-(^2D) \rightarrow Na(3d^2D) + Si(^3P)$ by up to 10% of the total cross section. Furthermore, we conclude that any contribution from the reaction $Na^+(1S) + Si^-(^2D) \rightarrow Na(5s^2D) + Si(^3P)$ would be even significantly smaller than that.

The results of both calculations agree that the $Na^+(1S) + Si^-(^2D) \rightarrow Na(4p^2P) + Si(^3P)$ reaction is the dominant one for metastable Si^- initial-state ions, but they differ in their predictions for the other two channels. Both calculations predict a contribution from $Na^+(1S) + Si^-(^2D) \rightarrow Na(3d^2D) + Si(^3P)$, which is significantly higher than the 10% upper limit we found experimentally, most dramatically for the calculations based on Olson's semiempirical couplings [33], where this channel is predicted to account for 47% of the cross section for metastable Si anions. Concerning the $Na^+(1S) + Si^-(^2D) \rightarrow Na(5s^2D) + Si(^3P)$ reaction, the semiempirical couplings by Olson [33] lead to a prediction of an insignificant contribution in accordance with our data, while the ACAM couplings [35] imply that 27% of the signal due to the metastables should be in this channel.

The signal that remains around 1.0 eV when the metastable beam component has been reduced by more than two orders of magnitude by laser photodetachment (see Fig. 3) is ascribed to the reaction labeled $Na^+(1S) + Si^-(^4S) \rightarrow Na(3p^2P) + Si(^1D)$. That means that the neutral formed by the removal of an electron from the anion is excited. This observation is

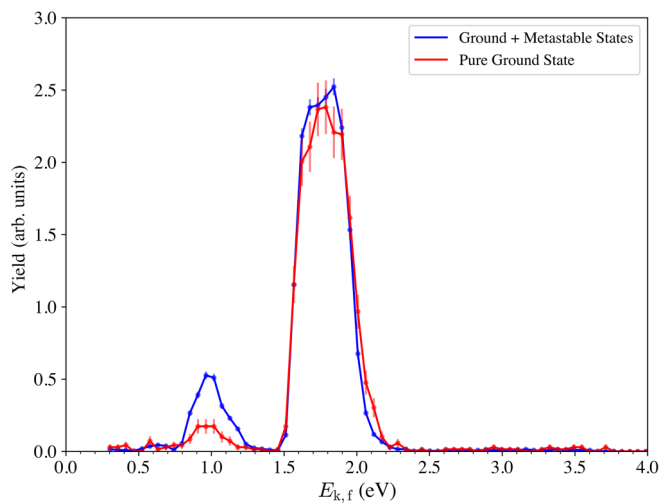


FIG. 4. Yield of neutral pairs as a function of total final channel center-of-mass kinetic energy $E_{k,f}$ for the reaction $Na^+ + Si^-$. Data shown in blue are recorded without laser use, and hence the metastable ^2D level is populated. The red curve is recorded after photodetachment elimination of the ^2D population.

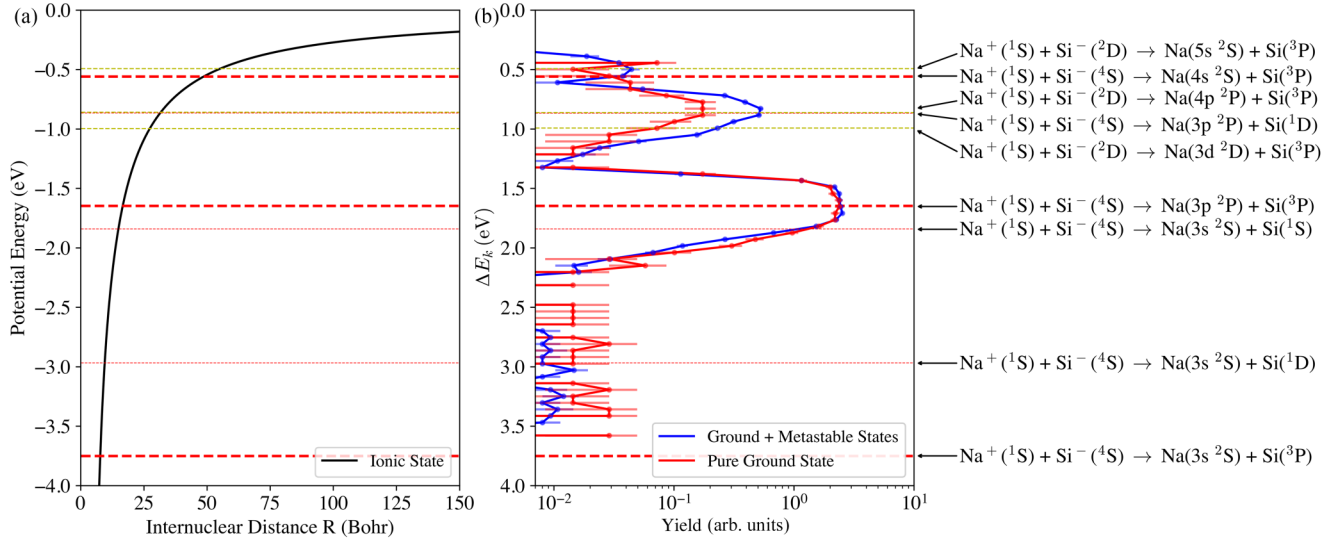


FIG. 5. Comparison of (a) diabatic potential-energy curves and (b) kinetic-energy-release ΔE_k spectra for mutual neutralization between Na^+ and Si^- . (a) Ionic potential (black solid line) along with horizontal lines indicating the asymptotic energy positions of the final neutral channels, referring to Si^- in either its ground state (red) or its metastable state (yellow). (b) Corresponding normalized ΔE_k distributions for mixed-state (blue) and pure ground-state (red) anion beams. Horizontal dashed lines denote the expected ΔE_k values: Red lines represent channels accessible when Si^- is in the ground state, while yellow dashed lines indicate contributions from the metastable $\text{Si}^-(^2D)$. Among the red dashed lines, long red dashes correspond to neutral silicon formed in the ^3P ground term, whereas short red dashes indicate channels producing Si in the excited ^1D and ^1S terms.

interesting from two different perspectives. From the experimental viewpoint, it is clear from Fig. 4 that it would not have been possible to observe this peak with a significant population of the metastable $\text{Si}^-(^2D)$ state. From a more fundamental point of view, it is surprising to see a significant contribution from this reaction. In most MN reactions, the anion takes part only as a donor of the electron and is not further excited. What makes this case particularly noteworthy is that the total electronic spin is not conserved, which explicitly violates the Wigner spin-conservation rule [17,18]. The excited neutral $\text{Si}(^1D)$ term results from pairing the two remaining $3p$ electrons from $\text{Si}^-(3p^3\ ^4S)$. The corresponding theoretical results based on the ACAM couplings [35] are based purely on LS coupling calculations and do therefore not include the possibility for the total spin to change from $3/2$ to $1/2$. Also, the calculations based on the Olson couplings do not include this channel.

B. MN with $\text{K}^+ + \text{Si}^-$

In Fig. 6 we show the MN data recorded for $\text{K}^+ + \text{Si}^-$. The data in red are recorded with a pure ground-state $\text{Si}^-(^4S)$ beam obtained through photodetachment, while the data in blue are recorded with a beam where also the metastable $\text{Si}^-(^2D)$ state is populated. The experimental conditions were optimized to achieve the highest possible energy resolution, allowing for clear identification of the individual reaction channels.

The dominant peak has a centroid value of (1.378 ± 0.014) eV and we ascribe it to the $\text{K}^+(^1S) + \text{Si}^-(^4S) \rightarrow \text{K}(4p\ ^2P) + \text{Si}(^3P)$ reaction channel with an expected kinetic-energy release of 1.341 eV and deduce an average initial kinetic energy of (0.037 ± 0.014) eV. Thus, we conclude that the by far dominating contribution to the MN signal arises from the

reaction $\text{K}^+(^1S) + \text{Si}^-(^4S) \rightarrow \text{K}(4p\ ^2P) + \text{Si}(^3P)$, where the active electron is captured to the $4p$ level of K with the Si atom formed in its ground state ^3P . As seen in Table II, calculations based on the ACAM couplings [35] and the Olson couplings [33] both predict this channel to be dominant.

Figure 7 compares the diabatic potential-energy curves with the ΔE_k spectra for the MN process between K^+ and

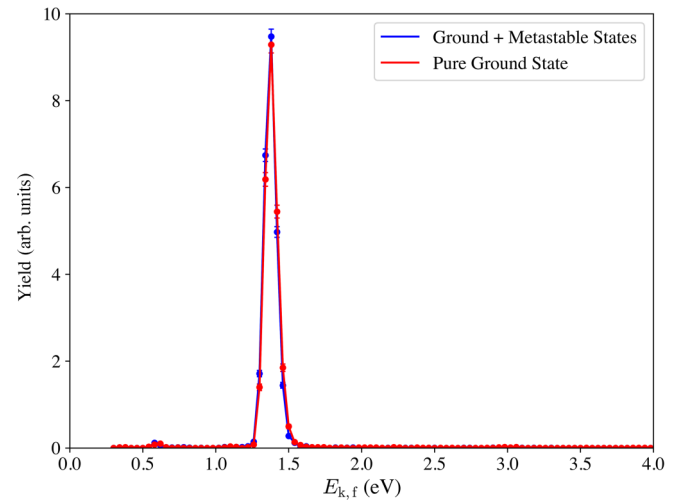


FIG. 6. Yield of neutral pairs as a function of final total center-of-mass kinetic energy $E_{k,f}$ for the reaction $\text{K}^+ + \text{Si}^-$. The blue data are from measurements without laser use, where the metastable levels (^2D) of Si^- are populated. The data shown in red are recorded after the elimination of the ^2D population by laser photodetachment. These data are also presented in Fig. 7 with a logarithmic y axis revealing weaker reaction channels.

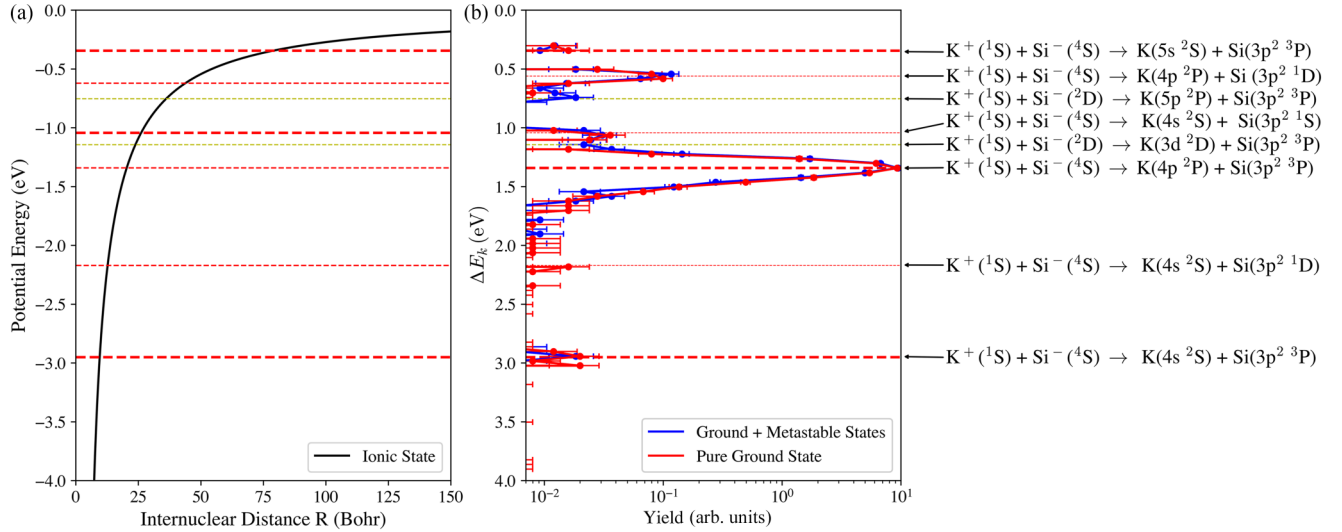


FIG. 7. Comparison of (a) diabatic potential-energy curves and (b) kinetic-energy-release ΔE_k spectra for mutual neutralization between K^+ and Si^- . (a) Ionic potential (black solid line) along with horizontal lines indicating the asymptotic energy positions of the final neutral channels, referring to Si^- in either its ground state (red) or its metastable state (yellow). (b) Corresponding normalized ΔE_k distributions for mixed-state (blue) and pure ground-state (red) anion beams. Horizontal dashed lines denote the expected ΔE_k values: Red lines represent channels accessible when Si^- is in the ground state, while yellow dashed lines indicate contributions from the metastable $Si^-(^2D)$. Among the red dashed lines, long red dashes correspond to neutral silicon formed in the ^3P ground term, whereas short red dashes indicate channels producing Si in the excited ^1D and ^1S terms.

Si^- . To show the weaker reaction channels, the spectra are presented on a logarithmic scale. The vertical lines indicate the ΔE_k for the various reaction channels as shown to the far right in Fig. 7.

For the $K^+ + Si^-$ case, the contributions from the metastable $Si^-(^2D)$ population are very weak, and we see only very small differences when the laser is applied, corresponding to $K^+(^1S) + Si^-(^2D) \rightarrow K(3d^2D) + Si(^3P)$ and $K^+(^1S) + Si^-(^2D) \rightarrow K(5p^2P) + Si(^3P)$. The smaller relative contributions from the metastable beam component in the case of $K^+ + Si^-$ as compared to $Na^+ + Si^-$ are consistent with the predictions of the Landau-Zener calculations. According to those, the total cross section for MN between Si^- and Na^+ is more than an order of magnitude higher for metastable than ground-state Si^- . In contrast, the total MN cross section for Si^- in collisions with K^+ is similar for ground-state and metastable Si^- ions (see Tables I and II).

Based on Table II and the 37 meV average initial kinetic energy, we ascribe the peak at $\Delta E_k = 0.56$ eV to $K^+(^1S) + Si^-(^4S) \rightarrow K(4p^2P) + Si(^1D)$. This is similar to the observation for the case of collisions with Na^+ where a small peak corresponds to excitation of the Si atom to the ^1D term in a process where the total spin of the collision system is not conserved. The high resolution and the very low background allow us to detect even weaker channels in the $K^+ + Si^-$ case. We observe a weak but significant signal at about 3.0 eV corresponding to forming both neutral atoms in their ground states $K^+(^1S) + Si^-(^4S) \rightarrow K(4s^2S) + Si(^3P)$. This channel was included in the calculations based on the Olson couplings, but was found to be completely negligible there. As this channel is the one with highest kinetic-energy release, it is also the one occurring at the

shortest interatomic distance where the use of the asymptotic forms of the potentials for the ion and neutral pairs is most doubtful.

Interestingly, we have a small peak due to $K^+(^1S) + Si^-(^4S) \rightarrow K(4s^2S) + Si(^1S)$, i.e., capture to $4s$ with Si left in the ^1S state, while the few counts at $K^+(^1S) + Si^-(^4S) \rightarrow K(4s^2S) + Si(^1D)$ corresponding to $Si(^1D)$ and ground-state K cannot be considered statistically significant even at this low background level. Comparing the roughly equal, small contributions from $K^+(^1S) + Si^-(^4S) \rightarrow K(4s^2S) + Si(^3P)$ and $K^+(^1S) + Si^-(^4S) \rightarrow K(4s^2S) + Si(^1S)$ indicates that the non-spin-conserving process leading to $Si(^1S)$ products has a more favorable potential-energy curve crossing. The few counts observed at the $K^+(^1S) + Si^-(^4S) \rightarrow K(5s^2S) + Si(^3P)$ line are consistent with a contribution from capture to the $5s$ level. This is however very close to the estimated lower limit for measurable final total kinetic energies of 0.3 eV in the present experiment.

V. CONCLUSION

Our study has demonstrated, using the cryogenic double electrostatic ion-beam storage-ring facility DESIREE, the ability to control the excitation of atomic anions in mutual-neutralization processes. This was illustrated here for Si^- colliding with Na^+ and K^+ ions. We demonstrated initial-state control by elimination of metastable Si^- beam components by state-selective laser photodetachment. For the pure ground-state beams, we identified small but significant contributions from final-state channels with excited ^1D and ^1S terms in the Si atoms formed in MN processes. This is surprising as these channels do not conserve the total spin, which is

$S = 3/2$ in the initial state and $S = 1/2$ in the final states. We performed Landau-Zener calculations for both collision systems and for Si^- ions both in the ground state ^4S and in the metastable state ^2D . Two different approaches were used to calculate the ionic-covalent electronic couplings: One was based on the semiempirical expression by Olson [33] and one was based on an asymptotic linear-combination-of-atomic-orbitals approach [35]. The calculations reproduce the leading channels well, but do not consider possibilities for contributions from non-spin-conserving reactions. Such contributions are however found for both collision systems in the present experiments and are clear example of violations of Wigner's spin-conservation rule. We conclude that spin-forbidden reactions may contribute substantially to total mutual-neutralization cross sections at sub-eV collision energies.

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DATA AVAILABILITY

The data that support the findings of this article are openly available in Ref. [34].

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