# State-selective single and double electron capture in the collision of N<sup>4+</sup> with He

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Ab initio potential-energy curves and rotational and radial coupling matrix elements of the  ${}^{2}\Sigma^{+}$  and  ${}^{2}\Pi$  molecular states involved in the collision of N<sup>4+</sup> with He are determined by means of configuration interaction methods. In the 1–50-keV laboratory energy range, the total and the partial electron capture cross sections have been obtained using a semiclassical approach. Comparison with experiment shows the importance of the double capture channels.

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## I. INTRODUCTION

Low-energy electron capture by multiply charged ions with atomic targets such as hydrogen or helium, have been shown to be an important process in controlled thermonuclear fusion research and particularly, the study of reactions involving carbon, nitrogen, and more recently boron has been stimulated by the need of precise information about impurity ion behavior.

Nevertheless, few accurate theoretical studies have been made on the electron-capture process for N<sup>4+</sup>+He. Indeed, this is an extremely complex collision system involving numerous states to deal with. In this paper, in order to understand the charge-transfer process at keV impact energies, we have undertaken an *ab initio* theoretical treatment of the N<sup>4+</sup>(2s)+He(1s<sup>2</sup>) charge-transfer process taking into account beyond the entry channel  ${}^{2}\Sigma^{+}$ {N<sup>4+</sup>(2s)+He(1s<sup>2</sup>)}, all the  ${}^{2}\Sigma^{+}$  and  ${}^{2}\Pi$  states correlated to the single {N<sup>3+</sup>(2*l*2*l'*)+He<sup>+</sup>(1s)} levels as well as those correlated to the {N<sup>2+</sup>(2s<sup>2</sup>2p)+He<sup>2+</sup>} and {N<sup>2+</sup>(2s2p<sup>2</sup>)+He<sup>2+</sup>} double electron-capture channels.

Experimentally, translation energy spectroscopy has been used by McLaughlin *et al.* [1] to study the one-electron capture by  $4-28 \text{ keV N}^{4+}$  ions in collisions with helium. They have shown evidence of a  $\text{N}^{3+}(2p^2)^1S$  dominant product channel, with contribution of other  $\text{N}^{3+}(2l2l')$  channels at higher energies that could not be interpreted by their multichannel Landau-Zener (MCLZ) calculations. This system has also been investigated by Okuno, Soejima, and Kaneko [2], Hoekstra, Heer, and Winter [3], and Iwai *et al.* [4] who provided total cross sections for single and double electron capture.

Due to the complexity of the system and to the range of the collision energy concerned (4–28 keV) it seems reasonable not to take account of the translation of the center-of-mass effects. The radial coupling matrix elements between all pairs of states of the same symmetry have been taken into account as well as the rotational coupling  $\langle \Psi_K | iL_y | \Psi_L \rangle$  matrix elements between the  $\Sigma$  and  $\Pi$  states. The collision dynamics has been performed by means of semiclassical methods using the EIKONXS algorithm.

## **II. MOLECULAR CALCULATIONS**

The one-electron and two-electron capture processes have been shown experimentally to be dominant, respectively, on  $N^{3+}(n=2)$  and  $N^{2+}(n=2)$  levels with a preponderant contribution on the { $N^{3+}(2p^2)^1S + He^+(1s)$ } one-electron channel [1,3]. From atomic data [5], this corresponds to very short curve crossing interactions, far shorter than possible curve crossings between the entry channel and the  $N^{3+}(2l3l') + He^+$  electron capture levels (Table I). It seems thus reasonable for this problem to neglect the capture on the  $N^{3+}(n=3)$  levels and calculate accurately the potential-energy curves in the inner region mainly, then extrapolate the potentials for larger internuclear distances by adding the Coulomb repulsion term.

The potential-energy curves and the nonadiabatic coupling matrix elements for the  $\Sigma$  and  $\Pi$  states have been calculated using the quantum-chemistry code MOLPRO [6]. The potential-energy curves have been thus determined accurately for a large number of inneratomic distances in the 1.2–5-a.u. range by means of a state-average CASSCF calculation using a direct algorithm [7,8] with configuration interaction. Considering the great number of states very close in energy that are involved in the problem, we could not

TABLE I. Asymptotic experimental energies [5] and crossing points for one- and two-electron collision capture channels in the  $N^{4+}(2s)^2S$  + He reaction.

Channel	Energy (a.u.)	$R_c$ (a.u.)	
$N^{4+}(2s)^2S + He$	1.9428		
$N^{3+}(2s3d)^{3}D + He^{+}$	1.9135	102.4	
$N^{3+}(2s3p)^{3}P + He^{+}$	1.8495	32.1	
$N^{3+}(2s3p)^{1}P + He^{+}$	1.8431	30.1	
$N^{3+}(2s3s)^{1}S + He^{+}$	1.7718	17.5	
$N^{3+}(2s3p)^{3}S + He^{+}$	1.7187	13.4	
$N^{3+}(2p^2)^1S + He^+$	1.0724	3.4	
$N^{2+}(2s2p^2)^2P + He^{2+}$	0.9218	3.9	
$N^{3+}(2p^2)^1D + He^+$	0.8606	2.8	
$N^{2+}(2s2p^2)^2S + He^{2+}$	0.8538	3.7	
$N^{3+}(2p^2)^3P + He^+$	0.8001	2.6	
$N^{2+}(2s2p^2)^2D + He^{2+}$	0.7171	3.3	
$N^{3+}(2s2p)^{1}P + He^{+}$	0.5955	2.2	
$N^{3+}(2s2p)^{3}P + He^{+}$	0.3065	1.8	
$N^{2+}(2s^22p)^2P + He^{2+}$	0.2574	2.4	
$N^{3+}(2s^2)^1S + He^+$	0.0	1.5	

TABLE II. Asymptotic energy values compared with experimental data [5] of the  $^2\Sigma$  and  $^2\Pi$  states of NHe^{4+}.

Channel	Experiment (a.u.)	Calculation (a.u.)
$\frac{1}{N^{4+}(2s)^2S + \text{He}(2\Sigma)}$	1.9428	1.9621
$N^{3+}(2p^2)^1S + He^+$ ( <sup>2</sup> $\Sigma$ )	1.0724	1.1006
$N^{2+}(2s2p^2)^2P + He^{2+}$ ( <sup>2</sup> $\Pi$ )	0.9218	0.9624
$N^{3+}(2p^2)^1D + He^+ (^2\Sigma, ^2\Pi)$	0.8606	0.8659
$N^{2+}(2s2p^2)^2S + He^{2+}$ ( <sup>2</sup> $\Sigma$ )	0.8538	0.8855
$N^{3+}(2p^2)^3P + He^+$ ( <sup>2</sup> $\Pi$ )	0.8001	0.8026
$N^{2+}(2s2p^2)^2D + He^{2+}$ ( $^2\Sigma, ^2\Pi$ )	0.7171	0.7341
$N^{3+}(2s2p)^{1}P + He^{+} (^{2}\Sigma, ^{2}\Pi)$	0.5955	0.6040
$N^{3+}(2s2p)^{3}P + He^{+} (^{2}\Sigma, ^{2}\Pi)$	0.3065	0.3040
$N^{2+}(2s^22p)^2P + He^{2+}$ ( $^2\Sigma, ^2\Pi$ )	0.2574	0.2695
$\frac{N^{3+}(2s^2)^1S + He^+}{2}$	0.0	0.0

extend our calculation to the complete active space selfconsistent field/multireference configuration interaction (CASSCF/MRCI) level, as the code is developed only for five states all together and the extension to a higher number of states induces inversion between levels. The calculation has been extended at the same level of theory until R=15 a.u. for the N<sup>3+</sup>(2*l*2*l'*), N<sup>2+</sup>(2*s*<sup>2</sup>2*p*), and N<sup>2+</sup>(2*s*2*p*<sup>2</sup>) levels. The basis of atomic functions used to represent N and He is the (16*s*,10*p*,5*d*,4*f*/6*s*,2*p*,1*d*) correlation-consistent polarized cc-pV6Z/VTZ basis set of Dunning [9]. In order to obtain maximum flexibility, we have not applied any contraction of the Gaussian primitives.

The asymptotic energy values extrapolated according to the Coulomb repulsion term are presented in Table II and are shown to be in a relative satisfactory agreement with the experimental data [5]. Only the  ${}^{2}\Sigma$  and the  ${}^{2}\Pi$  states have been considered since the entry channel is a doublet spin state.

The potential-energy curves for the  ${}^{2}\Sigma$  and the  ${}^{2}\Pi$  states of  $(NHe)^{4+}$  are displayed in Fig. 1. The  $^{2}\Sigma$  states show evidence of a very sharp avoided crossing around R = 3.7 a.u. between the entry channel and the  $\{N^{3+}(2p^2)^{1}S\}$ +He<sup>+</sup>} capture level corresponding to the dominant product channel as seen experimentally [1]. Broader avoided crossings are exhibited between the one-electron capture levels  $\{N^{3+}(2s^2)^1S + He^+\}$  and  $\{N^{3+}(2s^2p)^3P + He^+\}$  and be-tween the double capture channel  $\{N^{2+}(2s^22p)^2P + He^{2+}\}$ and the single charge-exchange level  $\{N^{3+}(2s2p)^{1}P\}$ +He<sup>+</sup>} around, respectively, 2.4 and 3.2 a.u. Furthermore, our calculation exhibits an intricate interaction region observable for 3.44-3.6 a.u. inner atomic distances corresponding to avoided crossings between the  $^{2}\Sigma$ states  $\{N^{3+}(2p^2)^1S + He^+\},\$  $\{N^{2+}(2s2p^2)^2S + He^{2+}\},\$ and  $\{N^{2+}(2s2p^2)^2D + He^{2+}\}$ levels as well the  $\{N^{3+}(2p^2)^{1}D + He^+\}$  channel by means of the long-range crossing between  $\{N^{2+}(2s2p^2)^2D + He^{2+}\}$ and  $\{N^{3+}(2p^2)^{1}D + He^+\}$ , which has been considered as quasidiabatic since it occurs at a relatively long-range internuclear distance.



FIG. 1. Adiabatic potential-energy curves for the  ${}^{2}\Sigma$  and  ${}^{2}\Pi$  states of (NHe)<sup>4+</sup>. 1:  ${}^{2}\Sigma$  state correlating to N<sup>3+</sup>(2s<sup>2</sup>)+He<sup>+</sup>(1s); 2:  ${}^{2}\Sigma$  and  ${}^{2}\Pi$  states correlating to N<sup>3+</sup>(2s<sup>2</sup>p)<sup>3</sup>P+He<sup>+</sup>(1s); 3:  ${}^{2}\Sigma$  and  ${}^{2}\Pi$  states correlating to N<sup>2+</sup>(2s<sup>2</sup>2p)<sup>2</sup>P+He<sup>2+</sup>; 4:  ${}^{2}\Sigma$  and  ${}^{2}\Pi$  states correlating to N<sup>3+</sup>(2s<sup>2</sup>p)<sup>1</sup>P+He<sup>+</sup>(1s); 5:  ${}^{2}\Pi$  state correlating to N<sup>3+</sup>(2s<sup>2</sup>p)<sup>2</sup>P+He<sup>2+</sup>; 4:  ${}^{2}\Sigma$  and  ${}^{2}\Pi$  states correlating to N<sup>3+</sup>(2p<sup>2</sup>)<sup>3</sup>P+He<sup>+</sup>(1s); 6:  ${}^{2}\Sigma$  and  ${}^{2}\Pi$  states correlating to N<sup>3+</sup>(2p<sup>2</sup>)<sup>2</sup>D+He<sup>2+</sup>; 7:  ${}^{2}\Sigma$  and  ${}^{2}\Pi$  states correlating to N<sup>3+</sup>(2p<sup>2</sup>)<sup>1</sup>D+He<sup>+</sup>(1s); 8:  ${}^{2}\Sigma$  state correlating to N<sup>2+</sup>(2s<sup>2</sup>p<sup>2</sup>)<sup>2</sup>S + He<sup>2+</sup>; 9:  ${}^{2}\Pi$  state correlating to N<sup>2+</sup>(2s<sup>2</sup>p<sup>2</sup>)<sup>2</sup>P+He<sup>2+</sup>; 10:  ${}^{2}\Sigma$  state correlating to N<sup>3+</sup>(2p<sup>2</sup>)<sup>2</sup>S+He(1s<sup>2</sup>) and 11:  ${}^{2}\Sigma$  state correlating to N<sup>4+</sup>(2s)<sup>2</sup>S+He(1s<sup>2</sup>) entry channel.

larly in the intricate region corresponding to R = 3.44-3.6 a.u. We find again crossings between  $N^{2+}(2s^22p)^2P + He^{2+}$  and  $N^{3+}(2s^2p)^1P + He^{+}$  around 3.2 a.u. and between  $N^{2+}(2s^2p^2)^2D + He^{2+}$  and  $N^{3+}(2p^2)^1D + He^{+}$  at long range around 7.8 a.u. Let us notice a short-range crossing between  $N^{3+}(2p^2)^3P + He^{+}$  and  $N^{3+}(2p^2)^1D + He^{+}$  around 2.5 a.u.

Such potential-energy curves show a very complex charge-exchange mechanism, including both single and double capture channels, which might be described by an extensive collision treatment.

The rotational coupling matrix elements  $\langle \Psi_K | iL_y | \Psi_L \rangle$ between the  $\Sigma$  and  $\Pi$  states have been determined by a state average CASSCF calculation including the nine  ${}^2\Sigma$  states and the seven  ${}^2\Pi$  states.

Considering the difficulties encountered in the CASSCF/ MRCI calculations using MOLPRO which leads to inversion of exited states that are very close in energy, we have recalculated the radial coupling matrix elements by means of multiconfiguration self-consistent field/configuration interaction (MCSCF/CI) calculations based on the configuration interaction by perturbation of multiconfiguration wave functions selected iteratively (CIPSI) algorithm [10]. Configuration interaction spaces used for the zeroth-order diagonalization Hamiltonian are, respectively, about 400/125 determinants for the  $\Sigma$  and  $\Pi$  levels. Special care has been taken to construct sets of determinants providing the same level of accu-



FIG. 2. Radial coupling matrix elements between  ${}^{2}\Sigma$  states of  $(NHe)^{4+}: 10-11, -; 8-10, --; 7-8, ...; 6-7: --- (labels)$ as in Fig. 1).

racy over the whole distance range with a threshold  $\eta$ =0.01 for the perturbation contribution to the wave functions.

The radial coupling matrix elements between all pair of states of the same symmetry have been calculated by means of the finite difference technique:

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$$g_{KL}(R) = \langle \Psi_K | \partial \partial R | \Psi_L \rangle$$
  
= 
$$\lim_{\Delta \to 0} \frac{\langle \Psi_K(R) | \Psi_L(R + \Delta) \rangle - \langle \Psi_K(R) | \Psi_L(R) \rangle}{\Delta}$$
  
= 
$$\lim_{\Delta \to 0} \frac{\langle \Psi_K(R) | \Psi_L(R + \Delta) \rangle}{\Delta}$$

according to the orthonormality of the  $\{\Psi_{K}(R)\}$  functions. For numerical accuracy, we have performed a three point numerical differentiation with calculation at  $R + \Delta$  and R $-\Delta$ . We have taken the parameter  $\Delta = 0.0012$  a.u. as previously tested [11] and used the nitrogen nucleus as the origin of the electronic coordinates in order to eliminate the spurious coupling terms at long range. The radial couplings for the  ${}^{2}\Sigma$  states are shown in Fig. 2. Sharp peaks may be observed in correspondence with the avoided crossings, in particular at about 4 a.u. for the radial coupling between the entry channel (channel 11) and the dominant exit channel  $N^{3+}(2p^2)^1S$  (channel 10).

#### **III. COLLISION DYNAMICS**

The collision dynamics has been treated by a semiclassical method using the EIKONXS program [12] based on an efficient propagation method in the 1-50-keV laboratory energy range, in order to be compared to the experimental data, in particular, the state selective translation energy spectros-



FIG. 3. Total and partial cross sections for  $N^{4+}$ +He.  $\times$ : experimental total cross sections [3,12]; +! experimental single electron capture cross sections [3,12]; \*: experimental double electron capture cross sections [3,12].

copy experiment of McLaughlin et al. [1] The total and partial cross sections are presented in Fig. 3. Our calculated total cross sections are shown to be in excellent agreement with those of Hoekstra, Heer, and Winter [3] tabulated by Wu, Huber, and Wiesmann [13]. As far as the single and double electron capture processes are concerned, the values of the cross sections are of the same order of magnitude, around  $2-3 \times 10^{-16}$  cm<sup>2</sup>, in satisfactory agreement with the experimental data although the theoretical calculations show a dominance of the double electron capture over single cap-



FIG. 4. Partial cross sections for  $N^{4+}$ +He compared to experimental results of McLaughlin et al. [1] o: peak A; \*: peak B; +: peak C; X: peak D.

TABLE III. Partial and total cross sections  $\sigma(10^{-16}\text{cm}^2)$ . Columns 2 to 5 correspond to the partial one-electron capture cross sections corresponding to curves A, B, C, and D of Fig. 4. Columns 6, 7, and 8 display, respectively, the total one-electron capture cross section, the two-electron capture cross sections, and the total cross sections.

E <sub>lab</sub> (keV)	$N^{3+}(2p^2)^1S$ ( $\Sigma$ )—A	$\begin{array}{c} \mathrm{N}^{3+}(2p^2)^1D + \\ \mathrm{N}^{3+}(2p^2)^3P \\ (\Sigma + \Pi) \mathrm{-\!-\!B} \end{array}$	$N^{3+}(2s2p)^{1}P$ ( $\Sigma+\Pi$ )—C	$N^{3+}(2s2p)^{3}P$ ( $\Sigma+\Pi$ )—D	$\sigma_{ m SC}$	$\sigma_{ m DC}$	$\sigma_{ m tot}$
3.5	1.9321	0.5127	0.0506	0.0078	2.5066	2.2507	4.7573
4	1.7818	0.5238	0.0372	0.0106	2.3572	2.2169	4.5741
14	1.0277	0.8681	0.1420	0.0254	2.0677	3.4727	5.5004
16	0.8702	0.8823	0.1443	0.0374	2.0944	3.6046	5.6990
22	0.6188	0.8272	0.0862	0.0595	1.9995	3.7313	5.7009
28	0.5033	0.7797	0.0921	0.0769	1.4657	3.6970	5.1627
31.5	0.4442	0.7962	0.1106	0.0830	1.4491	3.6563	5.1055
56	0.2053	1.1190	0.1702	0.2134	1.7453	3.2987	5.0444

ture, which is not evidenced by experimental data [3,4,13] taking into account the experimental error bar of about 25%-30% [3]. In agreement with McLaughlin's experimental results, the partial cross sections show clearly a decreasing feature with impact energy for the capture on the  $N^{3+}(2p^2)^{1}S$  channel corresponding to the dominant peak A. On the contrary, the partial cross section on  $N^{3+}(2p^2)^{1}D$  and  $N^{3+}(2p^2)^{3}P$ , corresponding to peak B, increases significantly with energy, in particular around 5-10-KeV impact energy, as well as the partial cross sections corresponding to peaks C, D, and E as also shown by the experimental results [1]. Let us note that the partial cross sections on channel  $N^{3+}(2s^2)^{1}S$  (peak E) remains always lower than  $10^{-18}$  cm<sup>2</sup>. Numerically, our partial cross sections can be compared to the experimental values of McLaughlin et al. [1] obtained by normalizing their results to the total electron capture cross section of Hoekstra, Heer, and Winter [3]. The results are displayed in Fig. 4 and Table III. A very good agreement is found for the partial cross sections corresponding to the capture on  $N^{3+}(2p^2)^{1}D$  and  $N^{3+}(2p^2)^{3}P$  (peak B); the calculated cross sections for  $N^{3+}(2p^2)^{1}S$  (peak A) show the same

decreasing shape as the experimental values but remain slightly underestimated. The partial electron capture cross sections on  $N^{3+}(2s2p)^{1}P$  (peak C) and  $N^{3+}(2s2p)^{3}P$  (peak D) are more difficult to compare with as there are fewer experimental points, nevertheless the increasing shape is globally reproduced.

### **IV. CONCLUSION**

This work provides a complete theoretical treatment of the single and double capture processes for the collision of N<sup>4+</sup> on He. Both processes are about the same order of magnitude. For the single capture process, our calculations identify clearly the dominant N<sup>3+</sup>(2p<sup>2</sup>)<sup>1</sup>S channel and predict significant cross sections for N<sup>3+</sup>(2p<sup>2</sup>)<sup>1</sup>D and to a lower extent for N<sup>3+</sup>(2p<sup>2</sup>)<sup>3</sup>P, N<sup>3+</sup>(2s2p)<sup>1,3</sup>P, and N<sup>3+</sup>(2s<sup>2</sup>)<sup>1</sup>S collision channels that involve crossings at small internuclear distances  $R_c$  with a very complex charge-exchange mechanism. Double capture channels are also significantly populated and compare positively to the experimental double capture process cross sections.

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