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Theoretical study of electron-capture processes in the collision of the metastable $N^{5+}(1s2s)$ multicharged ion on a He target

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The potential-energy curves and the radial coupling matrix elements of the $^3\Sigma^+$ and $^3\Pi$ states involved in the collision of the metastable $N^{5+}(1s2s)\,^3S$ multicharged ion on a helium target have been calculated by means of an *ab initio* method with configuration interaction. The partial cross sections of capture on the $3l$ levels have been determined using a semiclassical method and compared with experiment. The transfer-excitation process has been considered.

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I. INTRODUCTION

Electron capture on the ground state of multicharged ions from neutral atoms or molecules has been widely investigated both experimentally and theoretically. Nevertheless, metastable levels can be populated by foil excitation and electron capture on metastable states has been reported by photon spectroscopy [1–4] and electron spectroscopy [5–7]. From a theoretical point of view, such collisions involving metastable states have never been considered. This can scarcely be done by model potential methods most usually used in this field and requires *ab initio* calculations in order to determine the potential-energy curves of the states involved in the collision as well as the coupling matrix elements.

We report in this paper an *ab initio* molecular treatment on the electron-capture processes in the collision $N^{5+}(1s2s)+\mathrm{He}$. This is an example of a theoretical treatment of charge exchange involving metastable multicharged ions and this completes our previous study on the ground-state ion $N^{5+}(1s^2)$ in collision with helium [8,9].

This work has been undertaken in tight connection with experimental investigations regarding the $N^{5+}(1s2s)\,^3S+H_2$ and $N^{5+}(1s2s)\,^3S+\mathrm{He}$ collisions using photon spectroscopy at 60 keV [1,10] and electron spectroscopy at 51 keV [5].

From an experimental point of view, it is assumed that only the triplet metastable state $N^{5+}(1s2s)\,^3S$ will be involved in the collision because of the shorter lifetime of the singlet state [11] with respect to the time of flight of the ions from their production to the collision cell. Besides, among the doublet and quartet states $N^{4+}(1s2snl)\,^{2,4}L$ produced in the single-electron-capture process, the doublet states are rapidly autoionized, when the quartet states are metastable with respect to Coulomb autoionization and then transitions involving these quartet states may be observed. Nevertheless the experiment remains difficult because of the weakness of the observed lines and results are obtained with an error bar of at least 30%.

As in the case of the collision of the ground-state ion $N^{5+}(1s^2)$ on a He target, the main process has been shown experimentally to be the core-conserving single electron capture on the $n=3$ levels [5,10] with a small amount of capture on the $n=4$ levels. The transfer-excitation process corresponding to a single electron capture and an excitation of the core leading to $N^{4+}(1s2pnl)$ states has also been observed, with a dominance of the capture on the $3l$ levels [1,10].

Taking into account all the experimental contributions, we have considered in a theoretical investigation only the N^{4+} quartet states of single electron capture in the collision of the $N^{5+}(1s2s)\,^3S$ metastable ion on a He target. The capture being dominant on the $n=3$ levels, we have thus calculated the potential-energy curves for the entry channel $^3\Sigma^+[N^{5+}(1s2s)\,^3S+\mathrm{He}(1s^2)\,^1S]$ and the $^3\Sigma^+$ states of the $[N^{4+}(1s2s3l)\,^4L+\mathrm{He}^+(1s)\,^2S]$ configuration which are involved in the main process. We have also calculated the $^3\Sigma^+$ states corresponding to $[N^{4+}(1s2p3s)+\mathrm{He}^+(1s)]$ which could partly account for the transfer-excitation process. The corresponding $^3\Pi$ states have also been calculated as well as the radial coupling matrix elements between all the pairs of states of a given symmetry.

II. COMPUTATIONAL METHOD

The potential-energy curves for the $^3\Sigma^+$ and $^3\Pi$ states of interest have been calculated in the interatomic distance range 3.0 a.u. (4.0 a.u. for $^3\Pi$ states) to 20.0 a.u. (12.0 a.u. for $^3\Pi$ states) by means of an *ab initio* method with configuration interaction using the CIPSI (configuration interaction by perturbation of a multiconfiguration wave function selected iteratively) algorithm [12]. Relatively compact configuration-interaction (CI) spaces have been used in the calculation (261 determinants for the $^3\Sigma^+$ states and 203 for the $^3\Pi$ states) with a threshold $\eta=0.01$ for the perturbation contribution to the wave function leading to a quite large number of efficient states involved in the calculation (104 673 for $^3\Sigma^+$ levels and 92 228 for $^3\Pi$ levels).

The basis of atomic orbitals used in the calculation is presented in Table I. For helium, we have used the basis

TABLE I. Basis of atomic orbitals.

	N		He	
	Exponent	Coefficient	Exponent	Coefficient
s	6511.398 580	0.001 024	97.708 827	0.007 588
	1067.008 619	0.006 919	14.857 311	0.054 135
	265.065 942	0.030 818	3.373 390	0.215 948
	84.233 306	0.096 415	0.896 865	1.0
	12.670 187	0.353 890	0.250 773	1.0
	31.263 939	1.0	0.74	1.0
	6.880 613	1.0		
	4.038 833	1.0		
	2.511 393	1.0		
	1.131 746	1.0		
	0.506 687	1.0		
	0.240 800	1.0		
	0.105 581	1.0		
	0.015	1.0		
p	34.247 808	0.014 378	0.27	1.0
	9.075 274	0.074 986		
	3.054 122	0.263 691		
	1.182 084	1.0		
	0.545 175	1.0		
	0.302 031	1.0		
	0.093 545	1.0		
	0.019	1.0		
d	0.732	1.0		
	0.203 805	1.0		
	0.025	1.0		

previously constructed for the calculation of the $N^{5+}(1s^2)$+He collisional system [8]. For nitrogen we have used a 10*s*, 6*p*, 3*d* basis of Gaussian functions constructed from the 9*s*, 5*p*, 3*d* basis previously used in the $N^{5+}(1s^2)$ calculation, reoptimized on $N^{5+}(1s^2)$ for the *s* exponents and on $N^{4+}(1s^2 2p)$ for the *p* exponents, and added one *s* and one *p* diffuse function. The exponents of the most diffuse functions have been optimized with respect to the theoretical data of Chung [13] by means of a one-configuration calculation for the excited states of $N^{4+}(1s2s3l)$ and $N^{4+}(1s2p3l)$.

For such excited states, few experimental data are available, so we have compared the results of these optimization calculations with highly accurate atomic calculations taking into account relativistic correction terms [13]. The results are reported in Table II and show a rather reasonable agreement: the discrepancy is in the range 0.004 to 0.062 a.u. which gives of course a somewhat poorer accuracy than in our previous work on the ground-state $N^{5+}(1s^2)$ but we are dealing now with much higher excited states. Furthermore, the comparison with experimental data [14] for the transition $N^{5+}(1s^2)$

TABLE II. Comparison of present calculated atomic levels with experimental data [14] and other calculations [13] (in a.u.).

		Chung [13]		
	This calculation	Nonrelativistic	Relativistic	Experiment [14]
$N^{4+}(1s2s3d)\,^4D$	−30.832 782	−30.817 929	−30.837 461	
$N^{4+}(1s2s3p)\,^4P$	−30.864 605	−30.891 621	−30.911 482	
$N^{4+}(1s2s3s)\,^4S$	−30.992 015	−31.013 330	−31.033 845	
$N^{4+}(1s2p3d)\,^4F$	−30.594 964	−30.586 870	−30.604 060	
$N^{4+}(1s2p3p)\,^4D$	−30.729 597	−30.649 589	−30.667 166	
$N^{4+}(1s2p3s)\,^4P$	−30.798 135	−30.722 802	−30.740 776	
$N^{5+}(1s2s)\,^1S$	15.642 948			15.675 432
$N^{5+}(1s2s)\,^3S$	15.400 174			15.435 593
$N^{5+}(1s^2)\,^1S$	0.0			0.0

$\rightarrow N^{5+}(1s2s)\,^{1,3}S$ leads to a discrepancy of about 0.035 a.u., almost comparable to the precision of our previous calculation [8]. The comparison with relativistic atomic calculations gives besides an insight over the importance of relativistic terms which seem to be quite negligible with respect to the rate of accuracy reached in our calculation.

The radial coupling matrix elements $g_{KL}(R) = \langle \psi_k | \partial/\partial R | \psi_L \rangle$ between all pairs of states of the same symmetry have been calculated by means of the finite-difference technique [15],

$$g_{KL}(R) = \lim_{\Delta \to 0} \frac{1}{\Delta} \langle \psi_K(R) | \psi_L(R+\Delta) \rangle \ .$$

For reasons of numerical accuracy, we have performed a three-point numerical differentiation using calculations at $R-\Delta$ and $R+\Delta$ with a parameter $\Delta = 0.0012$ a.u. In order to estimate the importance of possible translation effects, calculations of $g_{KL}(R)$ have been carried out using both the N and He nuclei as the origin of electronic coordinates.

III. MOLECULAR RESULTS

The potential-energy curves of the five $^3\Sigma^+$ states and the three $^3\Pi$ states are presented in Fig. 1. The values of the nonadiabatic radial couplings are given in Table III for $^3\Sigma^+$ states and in Table IV for $^3\Pi$ states. The most important features of the radial coupling matrix elements between $^3\Pi$ states are sketched in Figs. 2(a) and 2(b).

TABLE III. Nonadiabatic radial coupling matrix elements between $^3\Sigma^+$ states (in a.u.).

R	g_{12}	g_{23}	g_{34}	g'_{45}
4.0	−0.026	1.903	−0.279	
5.0	0.527	0.711	−0.304	
5.3	0.920	0.121	−0.306	
5.4	0.997	0.076	−0.158	
5.5	0.945	0.041	0.029	
5.6	0.835	0.001	0.185	
6.0	0.052	0.122	0.729	
6.1	0.043	0.184	0.805	
6.4	0.045	0.588	0.076	
6.5	0.047	1.312	−0.228	0.178
6.6	0.072	1.353	−0.237	0.150
6.7	0.077	0.835	−0.253	0.122
7.0	0.029	0.142	−0.132	0.053
7.4	0.005	−0.059	1.056	0.004
7.5	0.002	−0.082	3.938	0.060
7.55	0.016	−0.144	8.717	0.120
7.6	0.021	−0.191	5.939	0.105
7.7	0.026	−0.213	1.115	0.016
8.0	0.102	−0.225	0.076	0.043
8.5	0.113	−0.336	0.051	0.049
9.0	0.102	−0.117	0.009	0.174
9.4	0.077	−0.123	−0.086	1.719
9.5	0.072	−0.150	−0.065	3.179
9.55	0.072	−0.184	−0.088	3.611
9.6	0.062	−0.204	−0.106	3.165
9.7	0.064	−0.217	−0.106	1.744
10.0	0.049	−0.203	−0.082	0.509
10.5	0.031	0.043	−0.023	0.258
11.0	0.026	0.008	0.0	0.017
20.0	0.0	0.0	0.0	

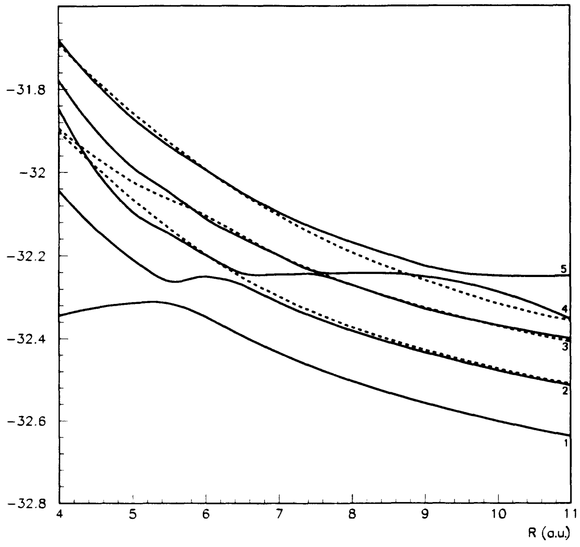

FIG. 1. Potential-energy curves of five $^3\Sigma^+$ states and three $^3\Pi$ states of NHe^{5+} metastable ion: ——, $^3\Sigma^+$ states; — — —, $^3\Pi$ states. 1: state dissociating to $\{N^{4+}(1s2s3s)+He^+(1s)\}$. 2: state dissociating to $\{N^{4+}(1s2s3p)+He^+(1s)\}$. 3: state dissociating to $\{N^{4+}(1s2s3d)+He^+(1s)\}$. 4: state dissociating to $\{N^{4+}(1s2p3s)+He^+(1s)\}$. 5: state dissociating to $\{N^{5+}(1s2s)\,^3S+He(1s^2)\,^1S\}$.

The potential-energy curves for the $^3\Sigma^+$ states show four avoided crossings in the range $5.0 \le R \le 10.0$ a.u. between the entry channel, the state corresponding to $[N^{4+}(1s2p3s)+He^+]$, and the three states corresponding to the $[N^{4+}(1s2s3l)+He^+]$ configuration. In relation to these avoided crossings, the radial coupling matrix elements present a sharp peak at, respectively 5.4, 6.6, 7.55, and 9.5 a.u. (Fig. 2). We may notice that the dominant radial couplings are quite insensitive to the choice of origin of electronic coordinates. The most sensitive function is the g_{23} radial coupling matrix element but since the sensitivity is only appreciable at short internuclear distances we may expect the influence of translation effects to be weak for electron-capture processes which are dominated by collisions for which the distance

TABLE IV. Nonadiabatic radial coupling matrix elements between $^3\Pi$ states (in a.u.).

R	g_{23}	g_{24}	g_{34}
4.0	0.204	0.044	0.002
5.0	0.351	0.070	0.123
6.0	0.101	0.060	0.204
7.0	0.063	0.020	0.051
8.0	0.087	0.033	0.044
9.0	0.135	0.056	0.039
10.0	0.055	0.053	0.005
11.0	0.048	0.042	0.004
12.0	0.037	0.025	0.030

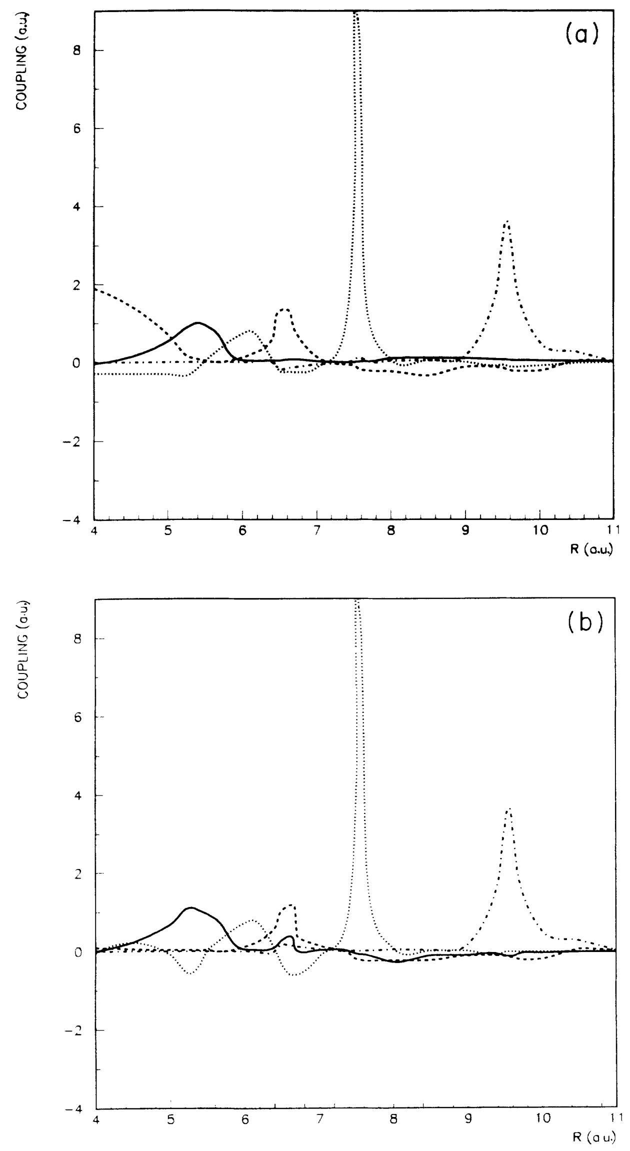

FIG. 2. Nonadiabatic radial coupling matrix elements between $^3\Sigma^+$ states. (a) origin O, (b) origin He. ——, g_{12}; — — —, g_{23}; · · · ·, g_{34}; —·—·—·, g'_{45} ($g_{45} \times 10$).

of closest approach is large.

The comparison of these results with those previously obtained for the $N^{5+}(1s^2)+He$ collisional system shows that all the crossings between the entry channel and the states of single electron capture are shifted towards shorter internuclear distances and have a lower height. But the main remark is related to the presence of an avoided crossing between the entry channel and the $^3\Sigma^+$ state corresponding to $[N^{4+}(1s2p3s)+He^+]$ which explains immediately the possibility of a transfer-excitation process for the $N^{5+}(1s2s)+He$ collision; such a process was not observed for the $N^{5+}(1s^2)+He$ collision.

The potential-energy curves for the $^3\Pi$ states show no evidence of avoided crossing and the corresponding radial coupling matrix elements are small and show very smooth variations.

IV. COLLISION DYNAMICS

The collision dynamics has been treated by semiclassical methods using the EIKONXS program [16] based on an efficient propagation method. In consideration with the experimental data available, the calculation has been performed for the collisional energies 60 and 50 keV. The radial coupling matrix elements between $^3\Pi$ states are very small for the whole internuclear distance range. Furthermore, it has been shown, from our calculation on the $N^{5+}(1s^2)+He$ collisional system, that the contribution of the Π levels coupled by the rotational couplings appears to be quite negligible over the contribution of the Σ levels coupled by the radial couplings for collision energies up to 50 keV. On this assumption, we have neglected, in a first calculation, the $^3\Pi$ states and performed the collisional treatment with the $^3\Sigma^+$ states only.

Two calculations have been performed: one with the entry channel and the three $^3\Sigma^+$ states of core-conserving single electron capture $[N^{4+}(1s2s3l)+He^+]$ and one including the transfer-excitation state. The partial cross sections of capture are presented in Table V and compared with the experimental results of Bouchama and Druetta [10] at 60 keV. Taking into account the experimental error bars, the agreement with experimental results seems to be fairly good. Our calculation gives confidence in the experimental results which are particularly difficult to analyze.

Besides, changing the origin of coordinates from the O nucleus to the He nucleus affects the partial cross sections by less than 20%, which is far behind the experimental error bar.

The same calculation performed at a collision energy of 50 keV let us compare the capture partial cross sections in the collision with He of both the ground $N^{5+}(1s^2)$ and the metastable $N^{5+}(1s2s)\,^3S$ multicharged ions. The results are presented in Table VI and show about the same magnitude for both systems with a value of the partial

TABLE V. Calculated values of the partial cross sections of capture at 60 keV. Comparison with experiment [10] (in 10^{-16} cm^2).

	O origin	He origin	Experiment [10] (±30%)
σ_{3s}	6.65	7.78	7
σ_{3p}	4.75	3.92	3
σ_{3d}	4.77	2.83	2
σ_{TE} $[N^{4+}(1s2p3s)+He^+]$	2.57	2.22	1.7

TABLE VI. Comparison of the capture partial cross sections with $N^{5+}(1s^2)$ and $N^{5+}(1s2s)\,^3S$ at 50 keV (in 10^{-16} cm^2).

	$N^{5+}(1s2s)\,^3S+He(1s^2)$		$N^{5+}(1s^2)+He(1s^2)$		
	Our calculation		Our calculation	Experiment	
	O origin	He origin	O origin	Ref. [2]	Ref. [17]
σ_{3s}	4.85	3.37	4.5	5.0	4.6
σ_{3p}	3.78	3.57	2.8	2.5	3.1
σ_{3d}	4.33	3.12	3.2	2.5	3.0

cross section on the 3*d* level slightly higher for the metastable ion. Such a result shows that neglecting the fraction of metastable ion in the ion beam will not lead to too high an experimental error.

V. CONCLUSION

This work provides accurate potential-energy curves and radial coupling matrix elements for a collisional system involving a metastable multicharged ion. The use of an *ab initio* method is necessary for an adequate representation of such an open-shell system with four outer electrons.

The agreement between calculation and experiment gives confidence both in the theoretical method used here and in the analysis of experimental spectra; in particular the interpretation of the transfer-excitation process is straightforward from the knowledge of the potential-energy curves of the collisional system.

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