

Electron-capture processes in the collision of metastable $B^{3+}(1s2s)$ on atomic hydrogen

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The potential-energy curves and couplings of the $^{2,4}\Sigma$ and $^{2,4}\Pi$ states involved in the collision of the metastable $B^{3+}(1s2s)$ multicharged ion on atomic hydrogen have been calculated by means of an *ab initio* method with configuration interaction. The collision processes have been examined, and the electron-capture cross sections have been determined by means of a semiclassical method.

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I. INTRODUCTION

As already mentioned in a previous paper [1], collisions from metastable levels have scarcely been tackled in previous theoretical studies, although the influence of metastable states in the incident beam has often been pointed out in experimental measurements [2,3]. For the collision of B^{3+} on atomic hydrogen, in particular, charge-transfer processes from the ground state $B^{3+}(1s^2)$ have been widely investigated theoretically using both model-potential [4] or *ab initio* [5] molecular-structure calculations, but the influence of metastable levels in the comparison with experiment [6] has rarely been taken into account.

As part of a more general investigation on collisions involving boron ions [7], we report, thus, in this paper an *ab initio* molecular treatment on the electron-capture processes in the $B^{3+}(1s2s)+H(1s)$ reaction. Both $^{2,4}\Sigma$ and $^{2,4}\Pi$ states correlated to the $\{B^{3+}(1s2s)^{1,3}S + H(1s)^2S\}^{2,4}\Sigma$ entry channels have been considered in the molecular calculation. Nevertheless, according to radiative-decay measurements [8], only the $B^{3+}(1s2s)^3S + H$ entry channel has been considered in the following collisional treatment performed by means of semiclassical methods including electron-translation effects.

II. MOLECULAR-STRUCTURE CALCULATION

The potential-energy curves of the states of interest have been calculated in the interatomic distance range 1.5–20 a.u. 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 [9]. Relatively compact configuration interaction (CI) spaces have been used in the calculation (303 determinants for the $^{2,4}\Sigma$ states and 301 determinants for the $^{2,4}\Pi$ states) ensuring a fair description of the zeroth-order Hamiltonian with a threshold $\eta=0.01$ for the perturbation contribution to the wave function.

The basis of Gaussian functions used in the calculation has been determined from the basis set previously constructed for the $B^{4+}+H$ collisional system [7], reoptimized for boron at the SCF (Self Consistent-Field) variational level on $B^{3+}(1s^2)$ for the s exponents and on $B^{2+}(1s2p^2)$ for the p exponents. The exponents of the more diffuse functions have then been optimized at the CI level with respect to the experimental data [10] on $B^{3+}(1s2s)^{1,3}S$ and to the theoretical data of Chung and Bruch [11] on $B^{2+}(1s2s2p)$ and $B^{2+}(1s2p^2)$. The comparison of the present atomic energy level values with highly accurate atomic calculations, taking into account

TABLE I. Comparison of present calculated atomic levels with experimental [10] and theoretical [11] data (in a.u.).

	This calculation	Chung [11]	Experiment [10]
$B^{2+}((1s2s)^1S3s)^2S$	-15.282572	-15.225285	
$B^{2+}((1s2s)^3S3s)^2S$	-15.364829	-15.343493	
$B^{2+}(1s2p2p)^2S$	-15.710209	-15.746105	
$B^{2+}(1s2p2p)^2D$	-15.898002	-15.922876	
$B^{2+}(1s2s2p)^2P$	-15.965813	-16.005377	
	-16.082655	-16.110491	
$B^{2+}(1s2s2p)^4P$	-16.250174	-16.272443	
$B^{2+}(1s2s2s)^2S$	-16.316379	-16.346215	
$B^{3+}(1s2s)^1S$	7.43936		7.45189
$B^{3+}(1s2s)^3S$	7.27845		7.29699
$B^{3+}(1s^2)^1S$	0.0		0.0

relativistic correction terms [11] as well as with experimental data [10], shows a rather reasonable agreement (Table I), in the range 0.012–0.057 a.u., quite comparable to that obtained in our previous calculation on $N^{5+}(1s2s)$ [1].

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

$$g_{KL}(R) = \lim_{\Delta \rightarrow 0} 1/\Delta \langle \Psi_K(R) | \Psi_L(R + \Delta) \rangle,$$

with the parameter $\Delta = 0.0012$ a.u., as previously tested [1,7] and using the boron nucleus as origin of electronic coordinates. The origin dependence has been taken into account in the collisional treatment by correcting, for each internuclear distance R , the radial coupling by the $(\epsilon_K - \epsilon_L)z^2/2R$ term (where ϵ_K and ϵ_L are the electronic energies of states Ψ_K and Ψ_L and z^2 a component of the quadrupole moment tensor), according to the common translation factor approximation developed by Errea, Mendez, and Riera [12]. The calculation of the

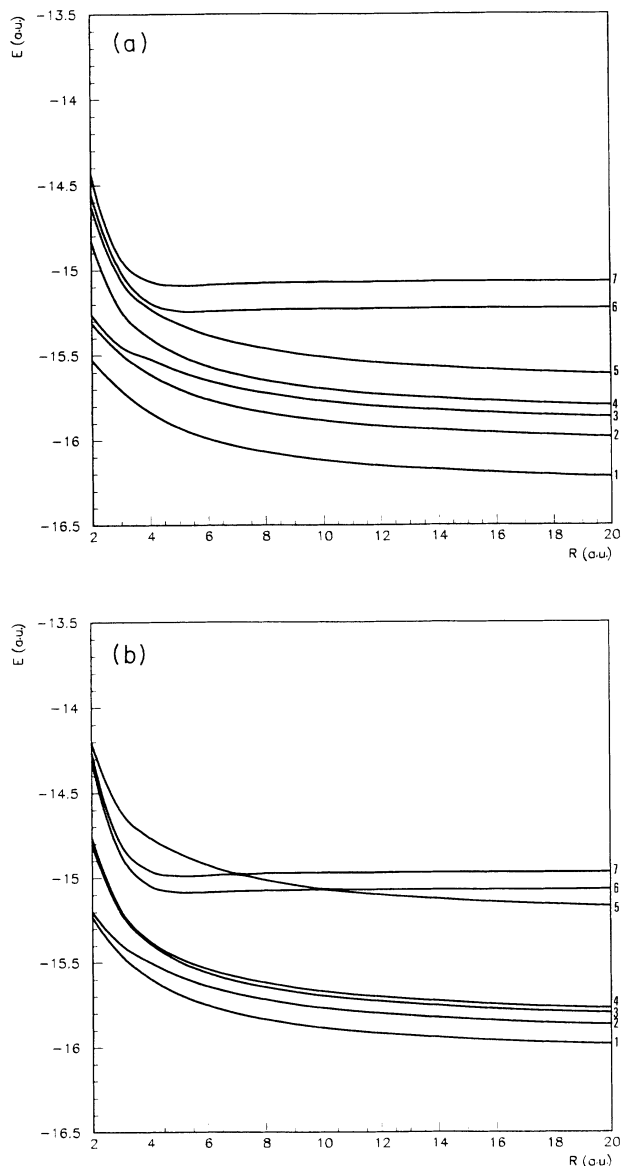


FIG. 1. (a) Lowest potential-energy curves of the ${}^2\Sigma$ states dissociating to 1: $\{B^{2+}(1s2s^2)+H^+\}$; 2 and 3: $\{B^{2+}(1s2s2p)+H^+\}$; 4 and 5: $\{B^{2+}(1s2p2p)+H^+\}$; 6: $\{B^{3+}(1s2s)^3S+H\}$; 7: $\{B^{3+}(1s2s)^1S+H\}$. Six and seven are entry channels. (b) Lowest potential-energy curves of the ${}^2\Pi$ states dissociating to 1 and 2: $\{B^{2+}(1s2s2p)+H^+\}$; 3 and 4: $\{B^{2+}(1s2p2p)+H^+\}$; 5: $\{B^{2+}(1s2s3p)+H^+\}$; 6: $\{B^{3+}(1s2p)^3P+H\}$; 7: $\{B^{3+}(1s2p)^1P+H\}$.

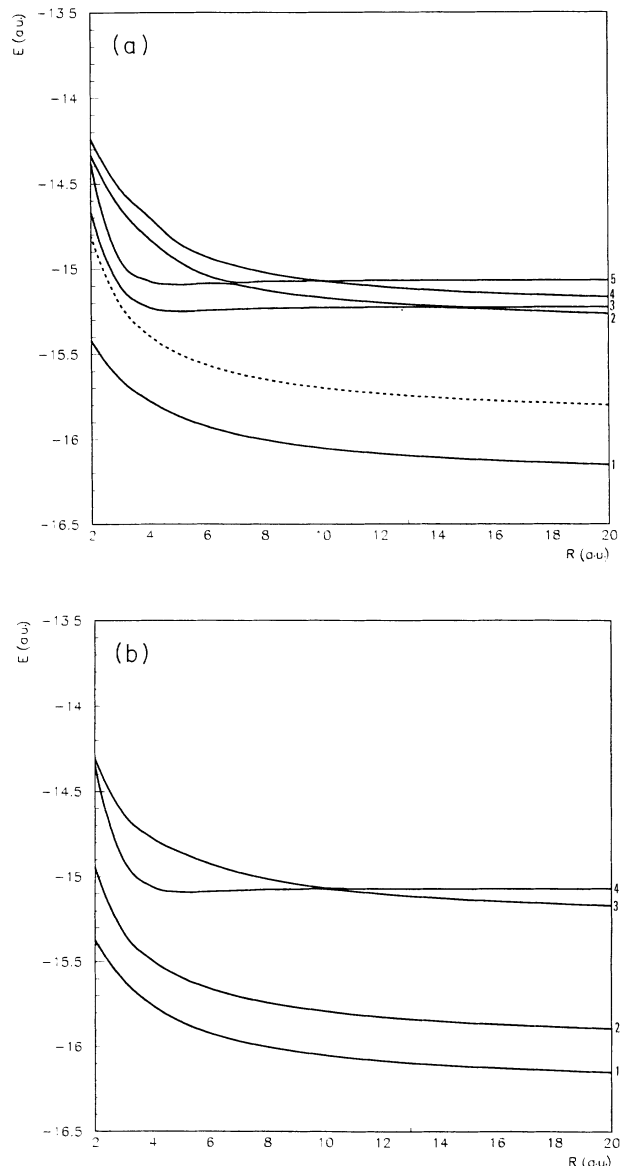


FIG. 2. (a) Lowest potential-energy curves of the BH^{3+} ${}^4\Sigma$ states dissociating to 1: $\{B^{2+}(1s2s2p)+H^+\}$; 2: $\{B^{2+}(1s2s3s)+H^+\}$; 3: $\{B^{3+}(1s2s)^3S+H\}$, entry channel; 4: $\{B^{2+}(1s2s3p)+H^+\}$; 5: $\{B^{2+}(1s2p3p)+H^+\}$. — — — ${}^2\Delta$ state dissociating to $\{B^{2+}(1s2p2p)+H^+\}$. (b) Lowest potential-energy curves of the ${}^4\Pi$ states dissociating to 1: $\{B^{2+}(1s2s2p)+H^+\}$; 2: $\{B^{2+}(1s2p2p)+H^+\}$; 3: $\{B^{2+}(1s2s3p)+H^+\}$; 4: $\{B^{3+}(1s2p)^3P+H\}$.

quadrupole-moment tensor allows also the direct determination of the rotational coupling matrix elements.

The potential-energy curves of the $2,4\Sigma$ and $2,4\Pi$ states are displayed, respectively, in Fig. 1(a),1(b) for doublet states and in Fig. 2(a),2(b) for quartet states. The most important features of the radial coupling matrix elements between states of the same symmetry are sketched, respectively, in Figs. 3 and 4 for doublet and quartet manifold.

The doublet manifold shows no evidence of any avoided crossing at large internuclear distances between the lowest 2Σ entry channel (channel 6) and any exit channel. The interaction between this entry channel and the $\{B^{2+}(1s2p2p)+H^+\}^2\Sigma$ state at lower internuclear distances (around 4.0 a.u.) remains smooth with a maximum of about 0.5 a.u. for the radial coupling. On the contrary, radial coupling matrix elements between 2Π states present sharp peaks in correspondence with the avoided crossings at $R=10.5$ a.u. between the $\{B^{2+}(1s2s3p)+H^+\}^2\Pi$ and the lowest $\{B^{3+}(1s2p)+H(1s)\}^2\Pi$ states, and at $R=7.0$ a.u. between the two $\{B^{3+}(1s2p)+H(1s)\}^2\Pi$ states.

The quartet manifold seems to be more important from a collisional point of view for two avoided crossings appear at an intermediate internuclear distance range involving the entry channel $\{B^{3+}(1s2s)+H(1s)\}^4\Sigma$ (channel 3): first a crossing with the $\{B^{2+}(1s2s3s)+H^+\}^4\Sigma$ exit channel (channel 2) at $R=14.9$ a.u., and a second one with the higher level dissociating to $\{B^{2+}(1s2s3p)+H^+\}^4\Sigma$ (channel 4) at $R=7.0$ a.u. The radial coupling matrix element g_{23} is particularly sharp, the corresponding crossing could be considered as purely diabatic in a collisional approach at intermediate energies. For both manifolds, the Π levels do not lie energetically close to the Σ states and the rotational coupling matrix elements remain small in the whole distance range. No important rotational effects could be evidenced.

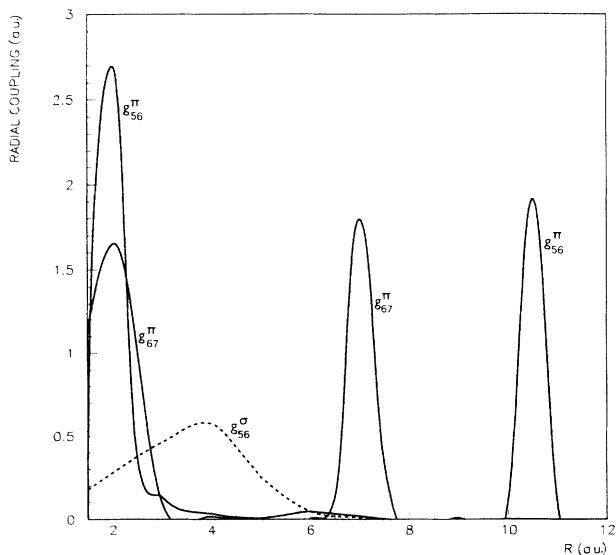


FIG. 3. Radial coupling matrix elements between doublet states. — — —: 2Σ states; —: 2Π states.

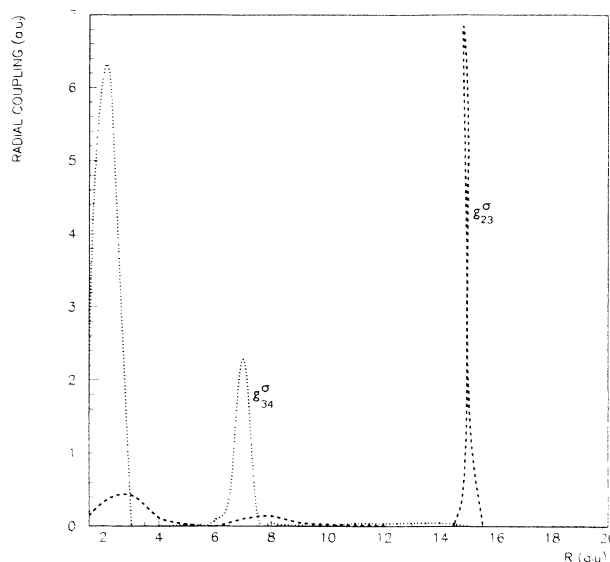


FIG. 4. Radial coupling matrix elements between quartet states.

III. COLLISION DYNAMICS

The collision dynamics has been treated by semiclassical methods using the EIKONXS program [13] in the $0.1-1.0 \cdot 10^8$ cm/s velocity range. As previously stated, the translation effects have been taken into account by introducing the common translation factors of Errea, Mendez, and Riera [12]. The coupled equations have been integrated separately for quartet and doublet states, taking into account Σ states only, and the cross sections have

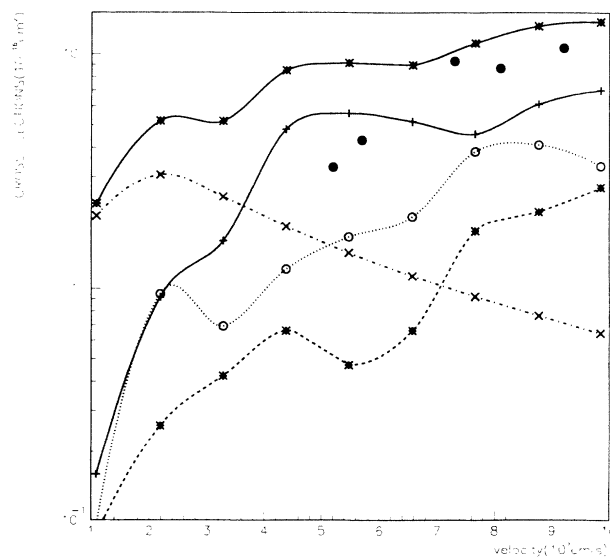


FIG. 5. Partial and total cross sections of capture from the $B^{3+}(1s2s)^3S+H$ entry channel. Quartet manifold: + —, Capture on $\{B^{2+}(1s2s3s)+H^+\}$; O · · ·, Capture on $\{B^{2+}(1s2p3p)+H^+\}$; * - - -, Capture on $\{B^{2+}(1s2s3p)+H^+\}$. Doublet manifold: X - - -, Capture on $\{B^{2+}(1s2p2p)+H^+\}$. * —, total cross section; ●, Experimental measurements on the ground state (Ref. [6]).

been determined according to the statistical weights $\frac{2}{3}$ and $\frac{1}{3}$, respectively. Considering the precedent discussion on molecular results, as well as the statistical weights, the charge-transfer process may be mainly driven by quartet states. As shown from the potential-energy curves, the charge-exchange process should be mainly driven at keV energies by the inner avoided crossing, the outer one being essentially diabatic. The calculation has, thus, been carried out with the assumption that the system pass through the outer crossing diabatically. The cross sections over the $B^{2+}(1s2s3s)$, $B^{2+}(1s2s3p)$, and $B^{2+}(1s2p3p)$ levels are displayed in Fig. 5. They show an oscillatory structure, quite comparable to that found by Olson, Shipsey, and Browne for the ground-state collision. Such a structure could certainly be related to the minima of potential-energy curves between the main channels. The $\{B^{2+}(1s2s3s)+H^+\}$ exit channel is dominant over a large range of collisional velocities, but at lower energies a competition appears with the doublet $\{B^{2+}(1s2p2p)+H^+\}$ channel which becomes even preponderant under $v_{\text{coll}}=0.35 \cdot 10^8$ cm/s and correspond to a quite short-range interaction. The total cross sections may be compared to the experimental data of Crandall, Phaneuf, and Meyer [6] for an incident beam composed *a priori* essentially of $B^{3+}(1s^2)$. The theoretical values are slightly higher than the experimental ones, mainly for velocities lower than $0.6 \cdot 10^8$ cm/s due to the influence of doublet states. On the contrary, for velocities in the range $0.6-1.0 \cdot 10^8$ cm/s they are quite of the

same order of magnitude as experimental measurements, as could be anticipated for such systems differing only by electronic configurations, and it is then justified to neglect the fraction of metastable in the beam. The error bar is always difficult to evaluate, especially in such problems considering excited potential-energy levels. In view of the correcting coupling term involved in the dynamics, the sensitivity to the origin of electronic coordinates could be estimated to less than 20%. Some further approximations have of course been made in order to simplify this quite complicated system, nevertheless the error bar could be estimated to about 30–40 %, as in many experimental measurements [2].

IV. CONCLUDING REMARKS

This work provides accurate potential-energy curves and coupling matrix elements for the collision of the metastable $B^{3+}(1s2s)$ multicharged ion on atomic hydrogen. *Ab initio* methods are required for such studies concerning open-shell systems with three outer electrons. From the present results, as well as from those previously obtained on $N^{3+}(1s2s)+He$, the neglect of the fraction of metastable in the beam seems to be reasonable at relatively high collisional energies.

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