

**Single and double electron capture in  $N^{5+} + H_2$  collisions at low impact energies**

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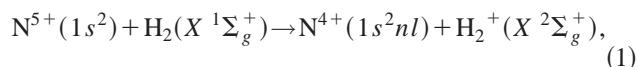
We present *ab initio* calculations of cross sections for single and autoionizing double electron capture in collisions of  $N^{5+}$  with  $H_2$ , for impact energies between 0.2 and 10 keV/amu. Calculations have been carried out by means of a close-coupling molecular treatment using the sudden approximation for rotation and vibration of the diatomic molecules. Since the molecular states involved are infinitely excited, a configuration interaction method, with a block-diagonalization procedure, has been employed to evaluate potential energy surfaces and dynamical couplings.

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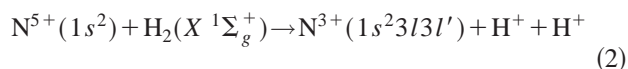
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**I. INTRODUCTION**

Electron capture processes in ion-molecule collisions are important reactions in the interaction of solar wind with cometary and planetary atmospheres (e.g., [1]) and fusion plasmas (e.g., [2]). In particular,  $N^{5+} + H_2$  collisions have been studied in both experimental and theoretical works. Photon emission spectroscopy [3,4] and translational energy spectroscopy [5] experiments have been carried out, and, as a general conclusion of these works, the most important processes at impact energies around 1 keV/amu are the single electron capture (SEC)



with  $n=3,4$ , and the autoionizing double capture (ADC)



reactions. However, the cross sections for the ADC reaction (2) were not directly measured in Ref. [5]; these were assumed to be equal to those for formation of  $N^{4+}(1s^22l)$ , which is the main product of the postcollision autoionization of  $N^{3+}$  after reaction (2).

Previous calculations [6,7] for this system employed a one-electron approach, where the “active” electron moves in the effective potential created by the nuclei and the remaining electrons; i.e., the  $N^{5+}$  and  $H_2^+$  cores. In particular, the pioneering work of Ref. [6] employed a model potential formalism, and a similar treatment, with pseudopotentials, was used in [7]. While an effective potential description of the electron interaction with the  $N^{5+}$  core is a good approximation, a similar treatment for the interaction with the open-shell  $H_2^+$  core is more questionable. In this respect, the calculation of Ref. [8] for  $H^+$  and  $Be^{4+}$  collisions with  $H_2$  showed that a two-electron interpretation of the transition probabilities, not performed in Refs. [6,7], is required to

evaluate single electron capture cross sections. Accordingly, a model potential treatment was applied to  $N^{5+} - H_2$  in a previous calculation of our group [9] including the two-electron interpretation, and assuming that the two target electrons are equivalent (see [10–12]). This approach is usually known as the independent electron approximation (e.g., in [13]) or independent particle model (IPM) (e.g., in [14]). An extension of the IPM was presented in [15], where the equivalent-electron interpretation was used to evaluate the Hamiltonian matrix elements rather than the transition probabilities, which allows extension of the range of applicability of the method to lower energies; this technique was applied to  $N^{5+} + H_2$  collisions in Ref. [16].

Although IPM treatments are appropriate to evaluate single electron capture cross sections, in general, they cannot accurately describe two-electron processes (see, e.g., [17] and references therein), and therefore it is difficult to justify the application of the IPM when those processes are sizable; this is the case of ion- $H_2$  collisions when double electron capture reactions are significant. However, for some particular collisions (see [15] and [18]), single and double electron capture take place through independent mechanisms, and the IPM yields accurate cross sections for single electron capture, although this can be checked only by comparison with all-electron calculations. The fact that only IPM calculations have been carried out for  $N^{5+} + H_2$  collisions, even though reactions (2) are expected to be competitive with (1), is mainly due to the difficulty of evaluating potential energy surfaces and dynamical couplings for the states of interest. The *ab initio* calculation of cross sections for reactions (1) and (2) is the main objective of the present paper.

An important difference between collisions of singly charged ions (see a recent example in Ref. [19]) and those of multicharged ions with  $H_2$  is the presence of infinitely excited states in the energy correlation diagram. In the particular case of  $N^{5+} + H_2$  (see Fig. 1), the energy of the entrance channel  $N^{5+}(1s^2) + H_2(X^1\Sigma_g^+)$  lies above the four Rydberg series  $N^{3+}(1s^22snl; 1s^22pnl) + H^+ + H^+$  and  $N^{4+}(1s^22s; 1s^22p) + H_2^+(n\lambda)$  (see Fig. 1), and the main electron capture channels [ $N^{4+}(1s^23l) + H_2^+(1\sigma_g)$ ] are also infinitely excited. Therefore, the molecular description of SEC involves transitions between states whose energies

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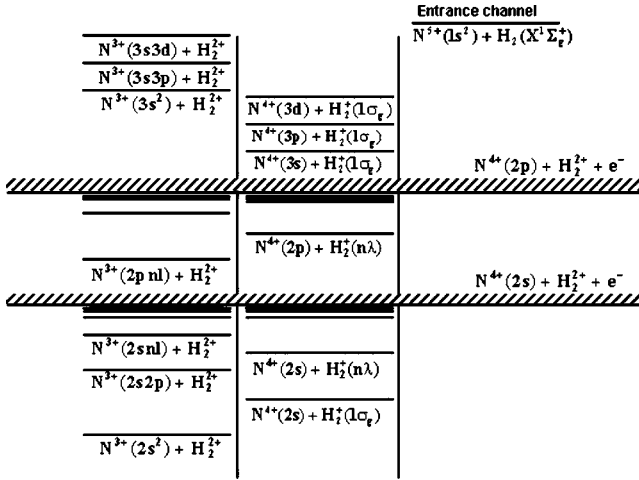


FIG. 1. Qualitative energy diagram of the asymptotic energies of the  $\text{NH}_2^{5+}$  quasimolecule.

lie in the ionization continuum. To calculate the potential energy surfaces and dynamical couplings, we have employed, as in previous work for  $\text{Be}^{4+}$  and  $\text{C}^{4+}$  collisions with  $\text{H}_2$  [20,21], block-diagonalization (BD) techniques [22], where the molecular states are obtained by diagonalizing the matrix of the electronic Hamiltonian in a basis from which the configurations that asymptotically correlate with the states of the Rydberg series are excluded. The main difference between the asymptotic energies of Fig. 1 with respect to those of the previously studied  $\text{C}^{4+} + \text{H}_2$  and  $\text{Be}^{4+} + \text{H}_2$  systems is that the energies of the ADC states  $\text{N}^{3+}(1s^23l3l')$  lie below that of the entrance channel, which in principle allows for sizable transitions to these states. In practice, this means that the entrance channel of the collision is a high-lying root of the secular equation even though the BD procedure is applied.

The paper is organized as follows: The details of the molecular calculation and the dynamical method are presented in Sec. II. Our results are shown in Sec. III and the main conclusions are outlined in Sec. IV. Atomic units are used unless otherwise indicated.

## II. METHOD

### A. Molecular calculations

The potential energy surfaces and molecular wave functions of the  $\text{NH}_2^{5+}$  quasimolecule are expressed in terms of the following relative nuclear coordinates: The distance from the  $\text{N}^{7+}$  nucleus to the center of the H-H internuclear axis,  $R$ , the H-H internuclear distance  $\rho$ , and the angle  $\alpha$  between the vectors  $\mathbf{R}$  and  $\boldsymbol{\rho}$ . Calling the set of electronic coordinates  $\mathbf{r}$ , the molecular wave functions  $\phi_j(\mathbf{r}; R, \rho, \alpha)$  are approximate eigenfunctions of the clamped-nuclei Born-Oppenheimer electronic Hamiltonian  $H_{\text{elec}}(\mathbf{r}; R, \rho, \alpha)$ :

$$H_{\text{elec}}(\mathbf{r}; R, \rho, \alpha) = \sum_{i=1}^4 \left( -\frac{1}{2} \nabla_i^2 - \frac{7}{r_{iN}} - \frac{1}{r_{iH1}} - \frac{1}{r_{iH2}} \right) + \sum_{i=1}^4 \sum_{j<i}^4 \frac{1}{r_{ij}}, \quad (3)$$

where  $r_{iN}$ ,  $r_{iH1}$ , and  $r_{iH2}$  denote the distances from electron  $i$  to the three nuclei.

The molecular wave functions are obtained using a self-consistent field (SCF)-configuration interaction (CI) method by means of the program MELD [23] and employing a basis set of Gaussian type orbitals.<sup>1</sup> In a first step, a SCF calculation is performed to obtain the molecular orbitals (MOs) of the  $\text{NH}_2^{7+}$  system. We have increased the molecular charge in this step to ensure that the unoccupied MOs (all except the ground MO) are good approximations to the orbitals of  $\text{N}^{4+}$  and  $\text{H}_2^+$  in the limit  $R \rightarrow \infty$ .

A configuration interaction is then carried out. For singlet states the configurations have the form

$$\psi_{kl} = \frac{1}{\sqrt{2}} [ || \xi_1 \bar{\xi}_1 \bar{\xi}_k \bar{\xi}_l || + || \xi_1 \bar{\xi}_1 \xi_l \bar{\xi}_k || ], \quad (4)$$

where  $\xi_j$  are MOs,  $|| \cdot ||$  denotes a Slater determinant, and where, to reduce the size of the CI space, we have applied the frozen core approximation in which the ground MO ( $\xi_1$ ) is always doubly occupied. To evaluate the wave functions for the entrance channel and the main exit channels, whose potential energy surfaces are infinitely excited (see Fig. 1), we have applied the block-diagonalization technique, originally proposed in [24], and applied to Multicharged ion collisions with  $\text{H}_2$  in Refs. [20] and [21]. In the present case, we employ the method to remove the molecular states dissociating as  $R \rightarrow \infty$  into those of the Rydberg series  $\text{N}^{3+}(1s^22s nl; 1s^22p nl) + \text{H}_2^{2+}$  and  $\text{N}^{4+}(1s^22s; 1s^22p) + \text{H}_2^+(n\lambda)$ , which is carried out by diagonalizing the matrix of the projected Hamiltonian  $PH_{\text{elec}}P$  with

$$P = 1 - \sum_{k=2}^5 \sum_{l=2}^N |\psi_{kl}\rangle \langle \psi_{kl}|, \quad (5)$$

where  $N$  is the number of MOs. The matrix representation of  $PH_{\text{elec}}P$  is obtained by removing from the CI space those configurations in which the MOs  $\xi_k$  with  $k=2,3,4,5$  are occupied, where the limits of these MOs, as  $R \rightarrow \infty$  are, to an excellent approximation, the  $2s$  and  $2p$  orbitals of  $\text{N}^{4+}$ .

As a check of the accuracy of the calculation, we compare in Table I the values of our molecular energies in the limit  $R \rightarrow \infty$  with the spectroscopic values [25] for  $\text{N}^{4+}$  and  $\text{N}^{5+}$  ions, and with accurate calculations [26] for the autoionizing states of  $\text{N}^{3+}$ . Cuts of the potential energy surfaces for  $\alpha=60^\circ$  are plotted in Figs. 2, 3, and 4 for  $\rho=1.0, 1.4$ , and  $1.7$  a.u., respectively. Except for  $\alpha=0$  or  $90^\circ$ , the system has  $C_s$  symmetry. Since the entrance channel of the collision transforms like  $A'$ , and only transitions to states of the same symmetry are allowed, we have included only states of  $A'$  symmetry in Figs. 2–4. An important detail of these energy curves is the sharp avoided crossings at large  $R$  between the energy of the entrance channel (e.c.) and those of the states dissociating into  $\text{N}^{3+} + \text{H}^+ + \text{H}^+$  in the limit  $R \rightarrow \infty$ . This sharpness is due to the fact that at large  $R$

<sup>1</sup>The basis set is available from the authors upon request.

TABLE I. Calculated differences of the energies (in a.u.) of several atomic states from that of  $N^{4+}(1s^2 3s)$ , compared with the spectroscopic values [25] for  $N^{4+}$  and  $N^{5+}$ , and accurate calculations [26] for the autoionizing states of  $N^{3+}$ .

State	Present work	Ref. [25]
$N^{4+}(1s^2 3s)$	0	0
$N^{4+}(1s^2 3p)$	0.0994	0.0989
$N^{4+}(1s^2 3d)$	0.1320	0.1289
$N^{4+}(1s^2 4s)$	0.6834	0.6842
$N^{4+}(1s^2 4p)$	0.7241	0.7244
$N^{4+}(1s^2 4d)$	0.7384	0.7369
$N^{4+}(1s^2 4f)$	0.7410	0.7378
$N^{5+}(1s^2)$	1.5172	1.5180
State	Present work	Ref. [26]
$N^{3+}(1s^2 3s^2)$	-1.2345	-1.2328
$N^{3+}(1s^2 3s 3p)$	-1.0986	-1.0834
$N^{3+}(1s^2 3s 3d)$	-1.0969	-1.0908

system has approximately  $C_{\infty v}$  symmetry, and the avoided crossings between the energies of states of different approximate symmetry ( $\Sigma$ -II,  $\Sigma$ - $\Delta$ , etc.) are very narrow. In practice, the states involved in narrow crossings exhibit  $\delta$ -function dynamical couplings between them, and the couplings of these states with the rest of the states change very rapidly in the avoided crossing region. Therefore, it is more convenient to employ a diabatic basis in the dynamical calculation, where the avoided crossings become crossings, as shown in Figs. 2–4. The diabatic states have been constructed by applying a technique [27] that is based on the evaluation of the delayed overlap matrix elements:

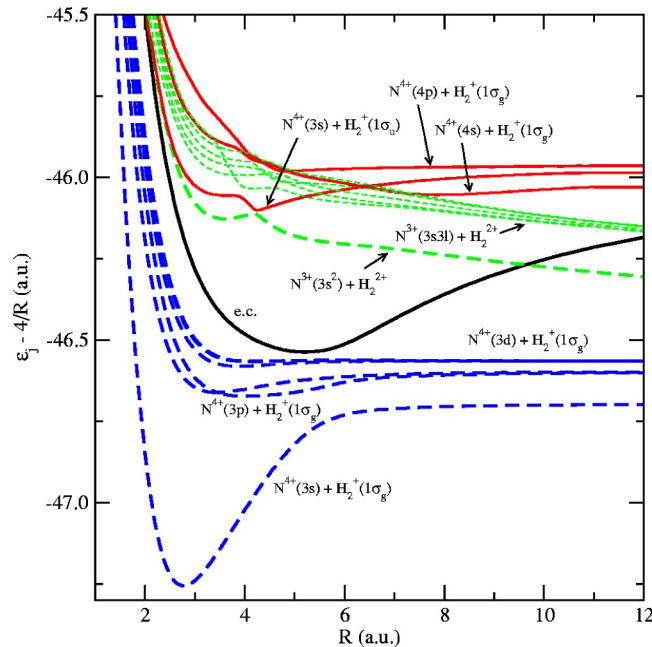


FIG. 2. Energies of the  $1A'$  electronic states of the  $NH_2^{5+}$  quasimolecule for  $\rho = 1.0$  a.u.

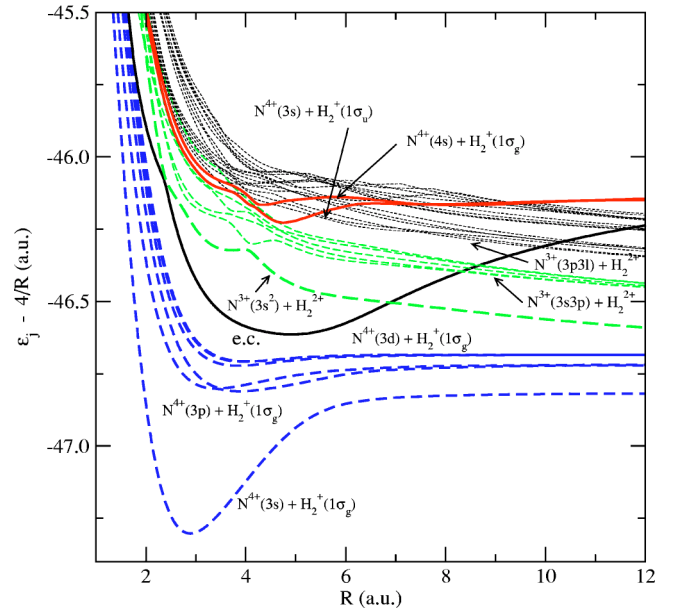


FIG. 3. Energies of the  $1A'$  electronic states of the  $NH_2^{5+}$  quasimolecule for  $\rho = 1.4$  a.u.

$$S_{jk}^* = \langle \phi_j(R_i) | \phi_k(R_{i+1}) \rangle, \quad (6)$$

where  $R_i$  and  $R_{i+1}$  are two adjacent points of the grid of internuclear distances. When  $|S_{j,j+1}^*|$  is larger than a given threshold value, we define two diabatic states  $\phi_j^d$  and  $\phi_{j+1}^d$  whose energies cross between the points  $R_i$  and  $R_{i+1}$ . In addition, the sign of the delayed overlap allows us to ensure that the sign of each molecular wave function is the same at all grid points.

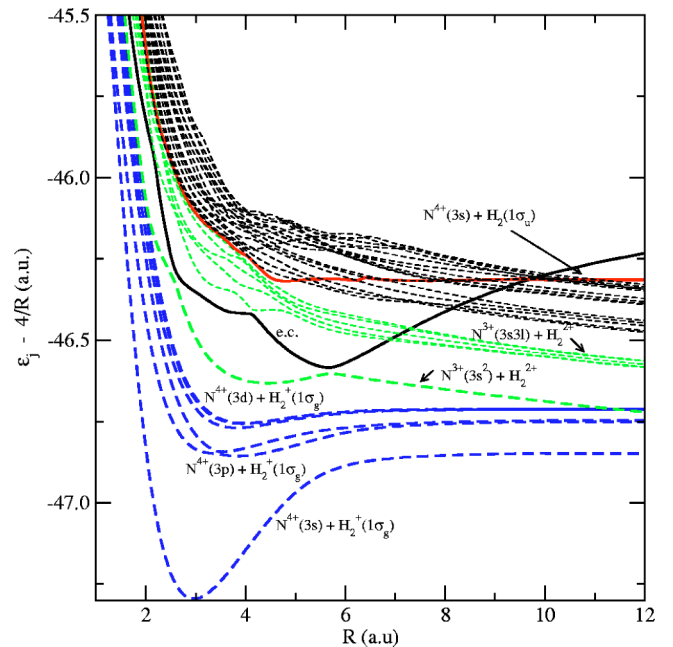


FIG. 4. Energies of the  $1A'$  electronic states of the  $NH_2^{5+}$  quasimolecule for  $\rho = 1.7$  a.u.

In Figs. 2–4, there is a sizable variation with  $\rho$  of the potential energy surfaces corresponding to the ADC states; they decay as  $1/\rho$  as  $\rho$  increases because of the  $H^+ \cdot H^+$  Coulomb interaction. This entails a variation in the position of the (avoided) crossings with the energy of the entrance channel (e.c.); in particular, the crossing between the e.c. curve and that of the  $N^{3+}(3s^2) + H^+ + H^+$  takes place at  $R \approx 9.5$  a.u. for  $\rho = 1.0$  a.u., at  $R \approx 6.5$  a.u. for  $\rho = 1.4$  a.u., and at  $R \approx 5.5$  a.u. for  $\rho = 1.7$  a.u.; in the last case the avoided crossing is wider and has not been diabaticized. Similar effects can be noted for the energies of the other double capture channels. A consequence of this  $\rho$  dependence of the ADC potential energy surfaces is that the identification of the SEC channels dissociating into  $N^{4+}(1s^2 4l) + H_2^+(1\sigma_g)$ , which is relatively easy at short  $\rho$  (see Fig. 2), becomes very difficult at  $\rho = 1.7$  (Fig. 4) because their energies show many avoided crossings with those of the ADC channels. In practice, this makes it very cumbersome to include molecular states correlating with  $N^{4+}(4l) + H_2^+$  in the dynamical calculation.

The main mechanism for SEC, indicated by the electronic energies of Figs. 2–4, involves transitions from the entrance channel to the low-lying states correlating with  $N^{4+}(3l) + H_2^+(1\sigma_g)$  at  $R = 4\text{--}5$  a.u., where the corresponding energies pseudocross. Since the crossings at large  $R$  are traversed diabatically, the main transitions to the ADC states take place at  $R < 3.0$  a.u. In the illustrations of Figs. 2–4, we have also drawn the energy of the state that diabatically correlates with the dissociative single electron capture state  $N^{4+}(3s) + H_2^+(1\sigma_u)$ ; this shows avoided crossings with those of the ADC states, and furnishes a mechanism whereby they can be depopulated.

### B. Dynamical method

The method employed in our dynamical calculation has been explained in previous work of our group. Its main assumptions are as follows.

(1) The impact parameter method (see, e.g., [17]), in which the position vector  $\mathbf{R}$  of the incident ion with respect to the target molecule follows straight-line trajectories  $\mathbf{R} = \mathbf{b} + \mathbf{v}t$  with constant velocity  $\mathbf{v}$  and impact parameter  $\mathbf{b}$ . The remaining degrees of freedom are treated quantum mechanically, by means of the wave function  $\Psi(\mathbf{r}, \boldsymbol{\rho}, t)$ .  $\Psi$  is a solution of the equation

$$\left( H_i - i \frac{\partial}{\partial t} \Big|_{\mathbf{r}, \boldsymbol{\rho}} \right) \Psi(\mathbf{r}, \boldsymbol{\rho}, t) = 0 \quad (7)$$

with  $\partial/\partial t = \mathbf{v} \cdot \nabla_{\mathbf{R}}$ ,

$$H_i = - \frac{1}{2\mu} \nabla_{\boldsymbol{\rho}}^2 + H_{\text{elec}}, \quad (8)$$

and  $H_{\text{elec}}$  is defined in Eq. (3).

(2) A close-coupling expansion in terms of the molecular wave functions  $\phi_j$ , which are approximate eigenfunctions of  $H_{\text{elec}}$  with energy  $\epsilon_j$ .

(3) The sudden approximation for rotation and vibration of the diatomic molecule, which assumes that the initial rovibrational wave function  $\chi_0(\rho) Y_{JM}(\hat{\boldsymbol{\rho}})$  does not appreciably change in the time interval in which the electronic transition takes place. One expands  $\Psi$  in the form

$$\begin{aligned} \Psi(\mathbf{r}, \boldsymbol{\rho}, t) = & \rho^{-1} Y_{JM}(\hat{\boldsymbol{\rho}}) \chi_0(\rho) \exp(iU) \\ & \times \sum_j a_j(t; \boldsymbol{\rho}) \phi_j(\mathbf{r}; \boldsymbol{\rho}, \mathbf{R}) \exp \left[ -i \int_0^t \epsilon_j dt' \right]. \end{aligned} \quad (9)$$

When  $\rho$  is fixed at the equilibrium H-H distance [ $\rho_0 \approx 1.4$  a.u. for  $H_2(X^1\Sigma_g^+)$ ] in the molecular wave functions of expansion (9), one obtains the familiar Franck-Condon (FC) approximation.

In the expansion (9),  $\exp[iU(\mathbf{r}, t)]$  is a common translation factor (CTF) [28], and in the present calculation we have employed the CTF of Ref. [29]. The expansion coefficients  $a_j(t; \boldsymbol{\rho})$  are obtained by substituting expansion (9) in Eq. (7). For fixed  $\boldsymbol{\rho}$  and for each nuclear trajectory these coefficients are solutions of the system of differential equations

$$\begin{aligned} i \frac{da_j}{dt} = & \sum_k a_k \left\langle \phi_j \exp(iU) \left| H_{\text{elec}} - i \frac{\partial}{\partial t} \right|_{\mathbf{r}, \boldsymbol{\rho}} \phi_k \exp(iU) \right\rangle \\ & \times \exp \left[ -i \int_0^t (\epsilon_k - \epsilon_j) dt' \right]. \end{aligned} \quad (10)$$

The cross section for transition to a given electronic channel is [30]

$$\sigma_f(v) = (4\pi)^{-1} \int d\mathbf{b} \int d\hat{\boldsymbol{\rho}} \int d\rho \chi_0^2 |a_f(\infty; \boldsymbol{\rho}_0) - \delta_{if}|^2. \quad (11)$$

Evaluation of the orientation averaged cross section of Eq. (11) requires one to solve the system of differential equations (10) for several orientations of the vector  $\boldsymbol{\rho}$  with respect to the nuclear velocity  $\mathbf{v}$ . Along the trajectory, the angle  $\alpha$  between vectors  $\mathbf{R}$  and  $\boldsymbol{\rho}$  changes, which in practice requires evaluation of the molecular wave functions  $\phi_j$  in a grid of values of this angle, and the ensuing two-dimensional interpolation of energies and couplings. A simplification of this procedure has been studied in previous work [30–32], where we have shown that a good approximation to the orientation averaged cross sections is given by an “isotropic” approximation, where the molecular wave functions of expansion (9) are assumed to vary little with  $\alpha$ , and one employs the molecular data calculated for an intermediate value (between  $45^\circ$  and  $60^\circ$ ). In this work we have used this “isotropic” approximation with  $\alpha = 60^\circ$ . Explicitly,

$$\begin{aligned} \sigma_f(v) = & 2\pi \int_0^\infty b P_f(b) db \\ = & \int_0^\infty d\rho \chi_0^2 \int_0^\infty b |a_f(\infty; \rho, \alpha = 60^\circ) - \delta_{if}|^2 db. \end{aligned} \quad (12)$$

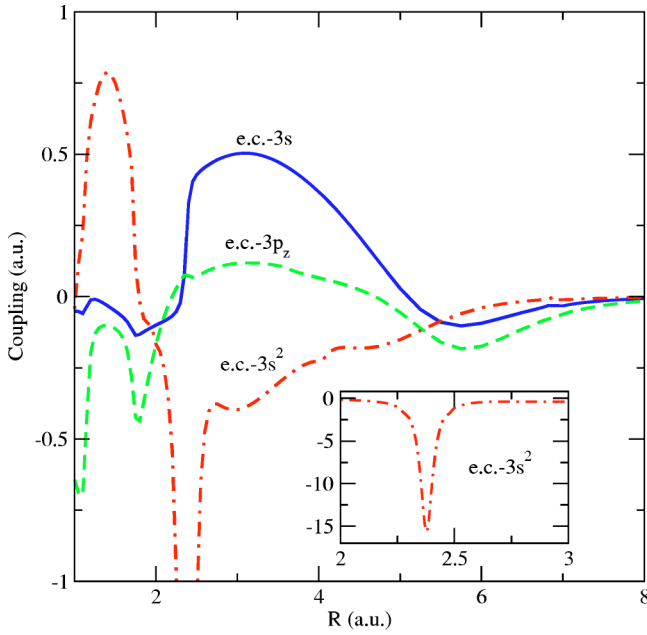


FIG. 5. Radial couplings between the entrance channel and the states correlating with  $N^{4+}(3s,3p)+H_2^+(1\sigma_g)$  and  $N^{3+}(3s^2)+H^++H^+$ , for  $\rho=1.4$  a.u. and  $\alpha=60^\circ$ . The inset shows the peak of the coupling between the entrance channel and the state correlating with  $N^{3+}(3s^2)+H^++H^+$ .

### C. Dynamical couplings

The transitions between the molecular states are induced by the nonadiabatic, or dynamical, couplings [see Eq. (10)], which can be expressed as (see, e.g., [18])

$$\begin{aligned} & \left\langle \phi_j \exp(iU) \left| H_{\text{elec}} - i \frac{\partial}{\partial t} \right| \phi_k \exp(iU) \right\rangle \\ &= \frac{v^2 t}{R} M_{ij} + \frac{bv}{R^2} R_{ij} + O(v^2). \end{aligned} \quad (13)$$

The translation factor introduces terms proportional to  $v^2$ , which have been neglected in the present calculation. The terms proportional to  $v$ ,  $M_{ij}$  and  $R_{ij}$ , are, respectively, the modified radial and rotational couplings, which have the forms

$$M_{ij} = \left\langle \phi_i \left| \frac{\partial \phi_j}{\partial R} \right|_{\alpha, \rho} \right\rangle + A_{ij}^R(R, \alpha, \rho) \quad (14)$$

and

$$R_{ij} = \left\langle \phi_i \left| \frac{\partial \phi_j}{\partial \alpha} \right|_{R, \rho} \right\rangle + A_{ij}^\alpha(R, \alpha, \rho), \quad (15)$$

where  $A_{ij}^{R, \alpha}$  are the corrections due to the common translation factor to first order in  $v$ .

As an illustration, we show in Fig. 5 the most important radial couplings [Eq. (14)] for  $\rho=1.4$  a.u. The main mechanism of the SEC reaction involves transitions from the entrance channel to the molecular states dissociating into

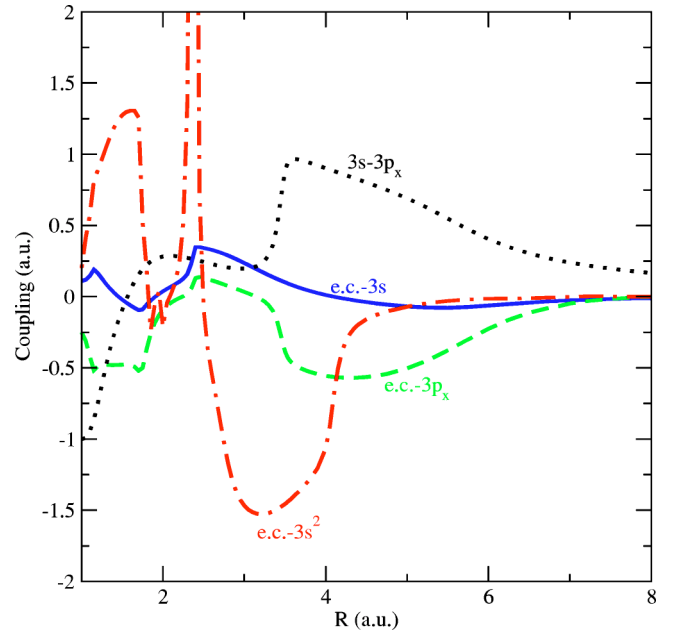


FIG. 6. Rotational couplings between the entrance channel and the states correlating with  $N^{4+}(3s,3p)+H_2^+(1\sigma_g)$  and  $N^{4+}(3s^2)+H^++H^+$ , for  $\rho=1.4$  a.u. and  $\alpha=60^\circ$ .

$N^{4+}(3s,3p)+H_2^+(1\sigma_g)$  in the wide avoided crossing at  $R \approx 4$  a.u., and where the corresponding radial couplings of Fig. 5 show relative maxima. Transitions from the entrance channel to the state correlating with  $N^{3+}(3s^2)+H^++H^+$  are the main mechanism of the ADC process; these transitions take place in the neighborhood of the avoided crossing at  $R \approx 2.37$  a.u., mainly induced by the tail of the radial coupling between these states. In turn, the rapid variation of the e.c. wave function in this region leads to an abrupt change of the radial couplings with the SEC states.

The structures of the most important rotational couplings [Eq. (15)], shown in Fig. 6, are related to the avoided crossings of Fig. 3. In particular, the avoided crossing at  $R \approx 3.5$  a.u. between the energies of the states correlating with  $N^{4+}(3p_x)+H_2^+(1\sigma_g)$  and  $N^{4+}(3p_z)+H_2^+(1\sigma_g)$  yields the abrupt changes of the e.c.- $3p_x$  and  $3s-3p_x$  couplings. The e.c.- $3s^2$  avoided crossing at  $R \approx 2.37$  a.u. leads to sharp peaks in both radial and rotational couplings. An avoided crossing at  $R \approx 2.00$  a.u. between the energy curves of the entrance channel and the highest SEC state correlating with  $N^{4+}(3l)+H_2^+(1\sigma_g)$ , which is difficult to notice in Fig. 3, causes the changes of the e.c.- $3s^2$  and e.c.- $3p_x$  couplings in this region.

### III. RESULTS

In a first step we employed the FC approximation and a basis set that includes 17 states with the following correlations in the limit  $R \rightarrow \infty$  (see Fig. 3): the entrance channel that correlates with  $N^{5+}+H_2(X^1\Sigma_g^+)$ ; the six states that correlate with  $N^{4+}(3l)+H_2^+(1\sigma_g)$ ; six states correlating with  $N^{3+}(3s3l)+H^++H^+$ ; one state correlating with  $N^{4+}(3s)+H_2^+(1\sigma_u)$ ; one state correlating with  $N^{4+}(4s)$

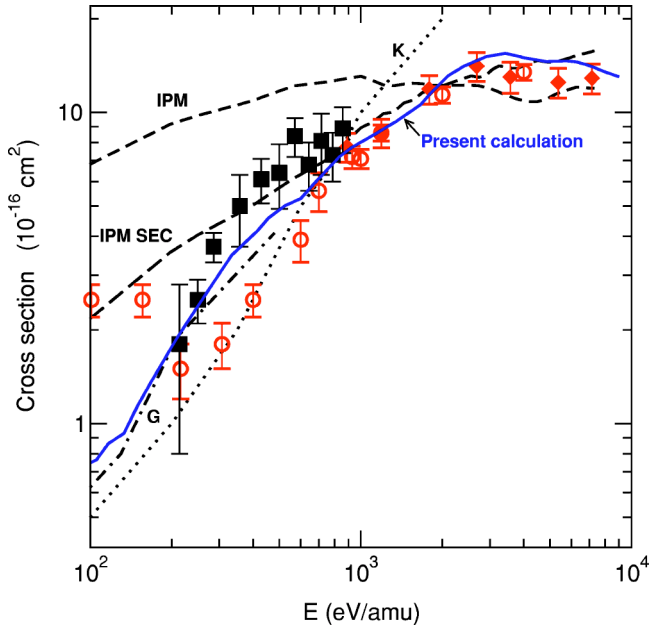


FIG. 7. Total cross sections for reaction (1): Calculations: —, present FC calculation; G, [6]; K, [7]; IPM, Ref. [9]; IPM-SEC, Ref. [16]. Experimental results:  $\blacklozenge$ , [3];  $\circ$ , [4];  $\blacksquare$ , [5].

$+H_2^+(1\sigma_g)$ ; and the two lowest states correlating with  $N^{3+}(3p3l)+H^++H^+$ .

The total cross sections for single capture are plotted in Fig. 7 together with the results of previous calculations at the FC level and experimental results. Our cross sections for single electron capture show good agreement with the experimental data of Kearns *et al.* [5], and reasonable agreement with the photon emission experiments of Refs. [3] and [4] for  $E > 200$  eV/amu. The usual IPM method is appropriate for  $E \geq 1.5$  keV/amu, while the modification of Ref. [15] (labeled IPM-SEC in Fig. 7) extends this range down to  $E \approx 700$  eV/amu. A good agreement at low  $E$  between the *ab initio* calculation and one-electron treatments [6,7] without two-electron interpretation was also found in [15,21] for  $C^{4+}+H_2$  collisions, and it was explained there as due to a compensation of errors because the effective potentials were fitted to the experimental  $H_2$  ionization potential instead of to the vertical one (for fixed  $\rho$ ).

An illustration of the mechanism of SEC and ADC reactions is shown in Figs. 8 and 9, where we have plotted the corresponding products  $bP_k(b)$  obtained in the FC calculation. At low  $E$  (Fig. 8), the calculation confirms the mechanism proposed in the previous section: the ADC process takes place at low  $b$  through transitions at  $R < 3.0$  a.u., induced by the e.c.- $3s^2$  radial coupling (see Fig. 5) in the neighborhood of the avoided crossing between the corresponding energy curves. At these low energies, the main mechanism of the SEC reaction involves transitions at larger  $R$  ( $\approx 4.0$  a.u.), where the couplings between the entrance channel and the states correlating with  $N^{4+}(1s^23l)+H_2^+(1\sigma_g)$  show relative maxima. On the other hand, the independent mechanisms of reactions (1) and (2), deduced from Fig. 8, explains (see Ref. [15]) the good agreement of

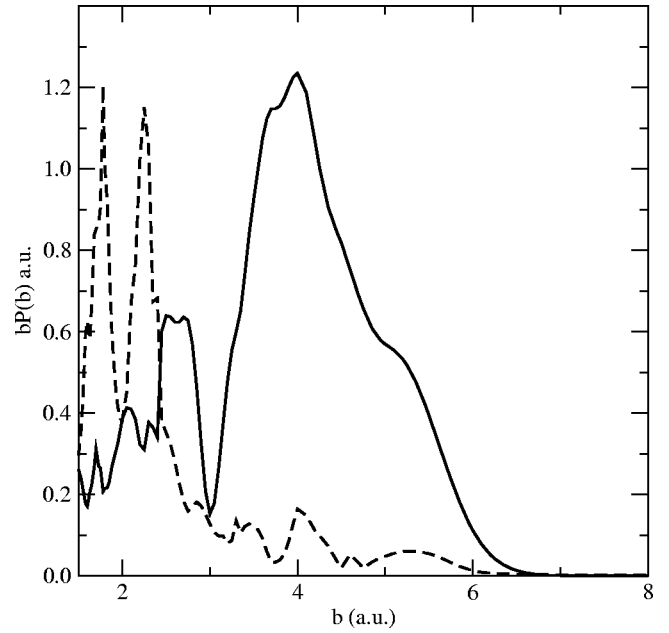


FIG. 8. Impact parameter times transition probabilities vs  $b$  for SEC into  $N^{3+}(n=3)$  (full line) and ADC into  $N^{4+}(3s3l)$  (dashed line), calculated using the FC approximation and for an impact energy  $E=500$  eV/amu.

the IPM-SEC results with the *ab initio* ones at  $E \approx 500$  eV/amu.

At high energies, the avoided crossing at  $R \approx 2.37$  a.u. is traversed diabatically, and the ADC transition probabilities do not show significant peaks at  $b < 3$  a.u., as illustrated in Fig. 9 for  $E=2$  keV/amu. The curves for SEC and ADC in Fig. 9 show maxima in the same regions of  $b$ , indicating that both reactions take place in the same regions of internuclear separations. Moreover, we have checked that the time evolu-

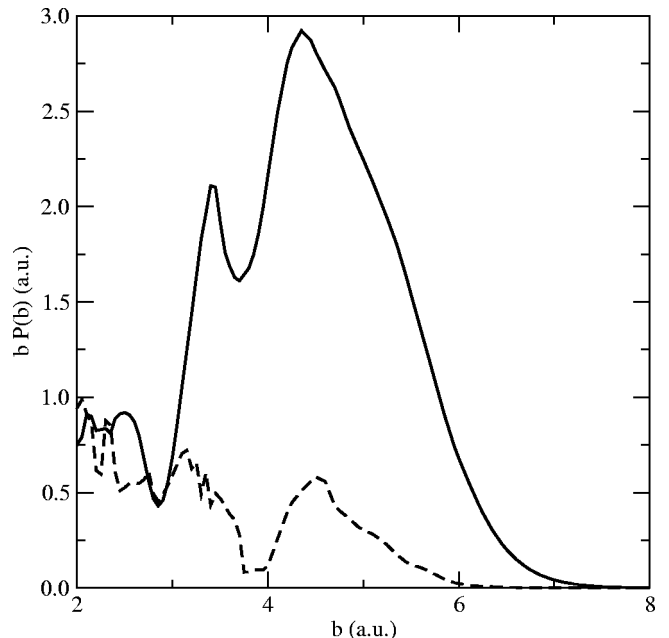


FIG. 9. Same as Fig. 8 for  $E=2$  keV/amu.

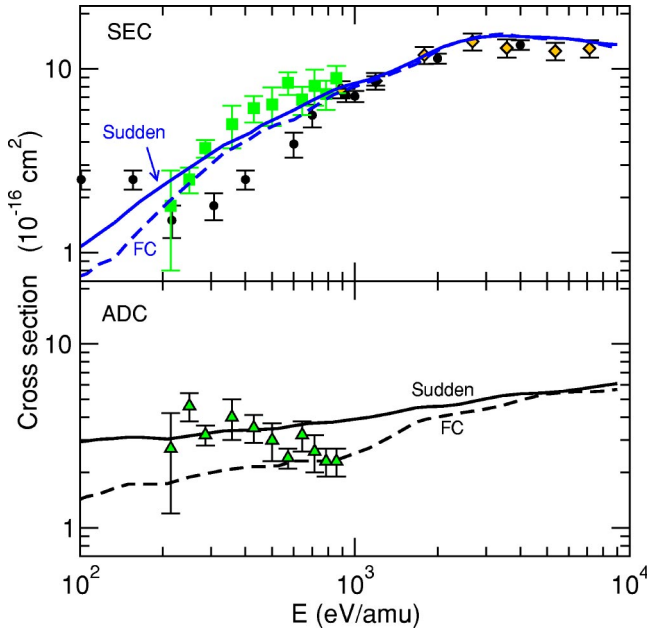


FIG. 10. Total cross sections for SEC (1) and ADC (2) reactions. Lines: present calculations, employing the sudden and FC approximations as indicated in the figure. Experimental results for SEC:  $\diamond$ , [3];  $\circ$ , [4];  $\blacksquare$ , [5]. Experimental cross sections for ADC:  $\blacktriangle$ , [5].

tion of the close-coupling coefficients suggests that ADC is now a two-step process through the SEC channels. At these energies, although the mechanisms are not independent, the populations of the ADC channels are relatively small, and, accordingly, the SEC transition probabilities are not strongly modified by the transitions leading to ADC, thus explaining the reasonable agreement of IPM and IPM-SEC cross sections with the experimental ones in Fig. 7. In this respect, a similar discussion was recently presented in Ref. [14] to explain the workings of the IPM approach for  $\text{He}^{2+} + \text{H}_2$  collisions.

We have also carried out non-FC dynamical calculations in the frame of the sudden approximation. We have checked that the cross sections of Fig. 7 do not appreciably change when the two  $\text{N}^{3+}(3p3l)$  states and the state correlating with  $\text{N}^{4+}(4s) + \text{H}_2^+(1\sigma_g)$  are not included. Therefore, in these calculations we employed a 14-state basis resulting from removing from the previous basis set these three states, which, as mentioned above, are difficult to include for  $\rho > 1.4$  a.u. Cross sections calculated within the vibrational sudden approximation for SEC into  $\text{N}^{4+}(3l)$  and ADC into  $\text{N}^{3+}(3s3l)$  are plotted in Fig. 10, where they are compared with those from the FC calculation and the experimental ones. In general, relatively small changes are observed between the two calculations for SEC, while the comparison with the experimental values for ADC is slightly better for the sudden approximation calculation than for the FC ones.

A more stringent test of the calculations is provided by comparison of the calculated partial cross sections for SEC with the photon emission measurements of Refs. [3,4]; this comparison is shown in Fig. 11, where we plot the ratios

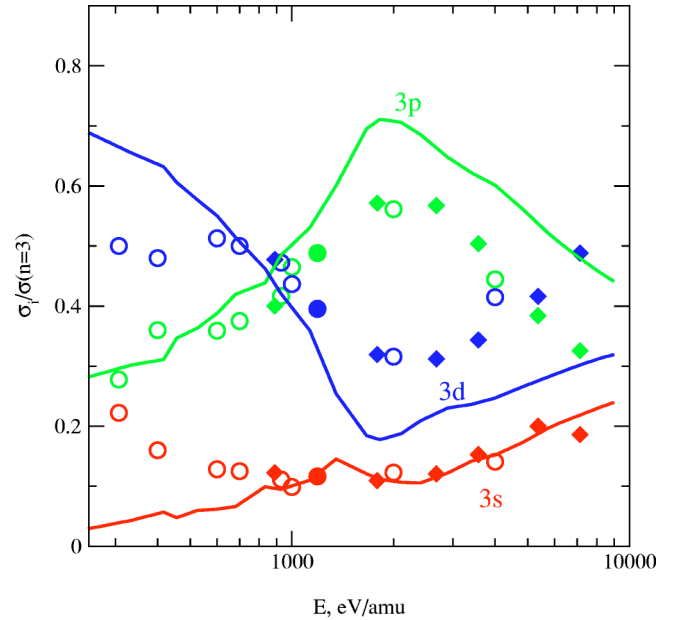


FIG. 11. Ratios  $\sigma(3l)/\sigma(n=3)$  of the partial cross sections for population of  $\text{N}^{4+}(n=3)$  levels in reaction (1). Lines, present results. Experimental results:  $\circ$ , [3];  $\blacklozenge$ , [4].

$$\gamma_{s,p,d} = \frac{\sigma_{s,p,d}}{\sigma_3}, \quad (16)$$

where  $\sigma_3$  is the total cross section for formation of  $\text{N}^{4+}(n=3)$  in the SEC reaction, and  $\sigma_{s,p,d}$  are the partial cross sections for formation of  $\text{N}^{4+}(3s, 3p, 3d)$  in the same reaction, evaluated in the frame of the sudden approximation. Although we find general good agreement between the experimental and calculated curves, some discrepancies can be noted at both low and high  $E$ , which are probably due to limitations of our calculation. In particular, at  $E > 6$  keV/amu, the calculated population of  $\text{N}^{4+}(3p)$  is larger than that of  $\text{N}^{4+}(3d)$ , which might be due to the lack of  $\text{N}^{4+}(n=4) + \text{H}_2^+$  channels. At  $E < 200$  eV/amu, the increase of the experimental total cross section in Fig. 10 is probably a consequence of transitions between vibronic states, which are not accurately taken into account by the vibrational sudden approximation; this can also cause of the already mentioned differences between theory and experiment for total cross sections at low  $E$  (Fig. 10).

#### IV. CONCLUSIONS

We have presented an *ab initio* calculation of SEC and ADC cross sections in collisions of  $\text{N}^{5+}$  ions with  $\text{H}_2$  at impact energies between 0.1 and 10 keV/amu, by applying the sudden approximation for vibration and rotation of the diatomic molecules. The energy range where our calculation is accurate is limited by the approximations employed. At low energies ( $E < 100$  eV/amu), the sudden approximation for vibration probably causes the discrepancy with photon emission measurements [4] between 100 and 200 eV/amu. At higher energies, the main limitation of our treatment is the truncation of the molecular basis set, and, in particular, the

lack of states correlating to  $N^{4+}(4l) + H_2^+(1\sigma_g)$  in that basis. Although we obtain good agreement with the experimental total SEC cross sections at  $E \approx 10$  keV/amu, the truncation of the basis set limits the validity of our calculation of SEC partial cross section to  $E < 5$  keV/amu.

With respect to the comparison with previous calculations that used the IPM approach, our cross section for SEC agrees with the IPM values for  $E > 2$  keV/amu, and the agreement extends to  $E > 700$  eV/amu for the IPM-SEC method of Ref. [15]. Our results also show good agreement with the recent experimental data of [5] in the energy range  $0.2 \leq E$

$\leq 1$  keV/amu for SEC into  $N^{4+}(n=3)$  and ADC. We have also found good agreement with the data of Refs. [3] and [4] for the branching ratio of  $3s$ ,  $3p$ , and  $3d$  levels of  $N^{4+}$  formed in the SEC reaction, in the energy range  $0.2 \leq E \leq 6$  keV/amu.

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