An ab initio calculation of the electron capture cross sections for collisions of ground and metastable states of N$^{2+}$ with H(1s) is presented. Total cross sections are evaluated for $^{14}$N impact energies from $2 \times 10^{-3}$ to 300 keV, using both quantal and semiclassical treatments. The results are compared with experimental and previous theoretical data, and are used to check the presence of metastable ions in the beams employed in the experiments. Partial cross sections are also presented and related to the collision mechanism.

I. INTRODUCTION

Electron capture (EC) in ion-atom (-molecule) collisions is important in astrophysical and fusion plasmas. However, the measurement of cross sections for these processes is often difficult due to the presence of unknown quantities of metastable species in the ion beam, and only recently have double translational energy techniques allowed measurement of EC cross sections for ions in both ground and metastable states (see [1,2]). In particular, N$^{2+}$ beams from the usual ion sources are, in principle, a mixture of unknown proportions of ground state ($2s^22p^1^P^o$) and metastable ($2s2p^2^P$) ions and, accordingly, the following EC reactions can take place in N$^{2+}$+H collisional experiments:

$$\text{N}^{2+}(2s^22p^1^P^o) + \text{H}(1s) \rightarrow \text{N}^+ + \text{H}^+, \quad (1)$$

$$\text{N}^{2+}(2s2p^2^P) + \text{H}(1s) \rightarrow \text{N}^+ + \text{H}^+. \quad (2)$$

Experimental work on this system includes the measurements of total EC cross sections of Refs. [3,4], carried out with a mixed beam, for $^{14}$N impact energies ($E$) in the range 8–600 keV. Translational energy experiments [5], which also used a mixed beam, yielded state-selective EC cross sections in the energy range 0.6–8 keV, extending the range to 200 keV for total EC cross sections. The use of the double translational energy spectroscopy technique allowed the energy change spectrum in EC to be recorded for an incident pure beam of ground state ions, at five collision energies between 0.8 and 6 keV [2]; these spectra showed three peaks at $\Delta E \approx 4.6, 2.5$, and $-2$ eV, corresponding to EC into N$^+(2s2p^1^D^o)$, N$^+(2s2p^3^P^o)$, and N$^+(2s^22p^33^P$ or $^3P^o$), respectively.

Pieksma et al. [6] carried out merged-beam measurements in a wide energy range $1.4 \times 10^{-3}$–62.2 keV. The measured total cross sections agree with previous experiments at $E > 30$ eV, but there are important disagreements at lower energies; e.g., differences of the order of 25% are found at $E \approx 10$ keV, and there is a shift to lower energies ($E \approx 2$ keV) of the local maximum found by Wilkie et al. [5] at $E \approx 5$ keV. This discrepancy is tentatively ascribed in [6] to the presence of vibrationally excited H$_2$ in the experiment of Ref. [5].

Theoretical works on N$^{2+}$+H collisions include the two-state calculation of Refs. [7,8], in the range of impact energies from $8.1 \times 10^{-5}$ to 80.4 keV. Herrero et al. [9] performed a quantal close-coupling calculation (triplets only) for $E < 1$ keV, which yielded total cross sections in reasonable agreement with the experimental data of Ref. [6], except for a maximum of the calculated cross section at $E \approx 4$ eV, not found in the experiment. Also, the energy dependence of cross section of Ref. [9] is completely different from the experimental one of Ref. [5] in the region $0.6 < E < 1$ keV.

The aim of the present paper is to present an extended close-coupling calculation of state-selective EC cross section for energies up to 300 keV. The calculation in the range $1 < E < 300$ keV, not covered by the work of Herrero et al. [9], requires the use of a large molecular basis set in order to consider collisions from both ground and metastable ions. In this energy region, we have employed the techniques previously applied to C$^{2+}$+H [10] and O$^{2+}$+H [11] collisions, which used a semiclassical treatment in terms of molecular expansions. For $E \approx 1$ keV, since there exists a discrepancy between measured and calculated total cross sections, and also between values from different experiments, we have employed both semiclassical and quantal treatments. This calculation is also relevant from the theoretical point of view since semiclassical and quantal results have been compared only for a few collisions. The energy region $0.002 < E < 1$ keV was covered by the calculation of [9] for reaction (1), but, given the sensitivity of the cross sections to the quality of the molecular data, we have extended the energy range down to 2 eV to check those results, in particular the different slope of the total cross sections when compared with the merged-beam results [6] and the above-mentioned maximum of the EC total cross section at $E \approx 4$ eV. In addition, the calculation of partial cross sections is particularly relevant at low energy, where present experimental techniques (merged-beam experiments [12]) yield only total cross sections, and new calculations have been recently carried out for one-electron systems (see Ref. [13] and references therein).
The paper is organized as follows. In Sec. II we summarize the dynamical (quantal and semiclassical) methods employed in the calculation. The details of the molecular calculation are presented in Sec. III and the dynamical calculations in Sec. IV. Our main conclusions are outlined in Sec. V. Cross sections are plotted as functions of \(^{14}\text{N}\) impact energy in keV. Atomic units are used unless otherwise indicated.

II. METHOD

A. Quantal treatment

For energies below 1 keV, we have applied a quantal treatment with a common reaction coordinate (CRC) [14,15]. In this section we only summarize the basis of the CRC method. A more detailed account of our implementation and references to previous works can be found in Ref. [16]. In the CRC treatment, the scattering wave function \(\Psi^J\) is expanded in a molecular basis set \(\{\phi_j\}\). For each value of the total angular momentum \(J\), one writes

\[
\Psi^J(\mathbf{r}, \xi) = \sum_k \chi_k^J(\xi) \phi_k(\mathbf{r}, \xi),
\]

where \(\mathbf{r}\) denotes the set of electronic coordinates and the functions \(\phi_k\) are approximate eigenfunctions of the clamped-nuclei electronic Hamiltonian:

\[
H_{\text{elec}} \phi_k(\mathbf{r}, \xi) = \epsilon_k(\xi) \phi_k(\mathbf{r}, \xi).
\]

In Eqs. (3) and (4), \(\xi\) is the CRC, which ensures that a truncated expansion satisfies the scattering boundary conditions; this coordinate is a combination of electronic and nuclear coordinates of the form

\[
\xi = \mathbf{R} + \frac{1}{\mu} \mathbf{s}(\mathbf{r}, R)
\]

with

\[
s = \sum_{\alpha=1}^{N_{\text{elec}}} \left[ f(\mathbf{r}_\alpha, R) \mathbf{r}_\alpha - \frac{1}{2} f^2(\mathbf{r}_\alpha, R) \mathbf{R} \right].
\]

In these expressions, \(\mu\) is the nuclear reduced mass, \(\mathbf{R}\) is the internuclear vector, \(N_{\text{elec}}\) is the number of electrons, \(\mathbf{r}_\alpha\) are the electronic position vectors, relative to the center of mass of the nucleus, and \(f\) is a switching function which satisfies

\[
\lim_{R \to \infty, \mathbf{r}_\alpha \to \text{finite}} f(\mathbf{r}_\alpha, R) = -p,
\]

\[
\lim_{R \to \infty, \mathbf{r}_\alpha \to \text{finite}} f(\mathbf{r}_\alpha, R) = q,
\]

where \(pR\) and \(qR\) are, respectively, the distances from nuclei \(A\) and \(B\) to the center of nuclear mass. It can be shown that, for any reaction channel, the CRC of expression (5) becomes the appropriate asymptotic interatomic coordinate to \(O(\mu^{-1})\). Substitution of the expansion (3) in the stationary Schrödinger equation yields a system of differential equations for the nuclear wave functions

\[
[(2\mu^{-1})^2 \nabla^2_\xi + (\mathcal{E} - \epsilon_j)] \chi_j^J + \sum_l [2\mu^{-1} \mathbf{M}_{jl} \cdot \nabla_\xi + (\phi_j(\xi^2) \phi_l)] \chi_j^J = 0,
\]

where \(\mathcal{E}\) is the impact energy in the center of mass reference frame. Terms proportional to \(v^2\) have been neglected in Eq. (8), and the modified dynamical coupling \(\mathbf{M}_{jl}\) is a vector whose \(q\) component has the form

\[
M_{jl}^q = \langle \phi_j | \frac{\partial}{\partial \xi_q} | \phi_l \rangle + A_{jl}^q
\]

with

\[
A_{jl}^q = \sum_{\alpha=1}^{N_{\text{elec}}} \langle \phi_j | \nabla_{\mathbf{r}_\alpha} (s_q) \cdot \nabla_{\mathbf{r}_\alpha} + \nabla^2_{\mathbf{r}_\alpha} | \phi_l \rangle.
\]

The form of the corrections \(A_{jl}\) depends on the particular switching function employed. In this work we have used that of [17]:

\[
f(\mathbf{r}, R) = \frac{R}{R^2 + \beta^2} \mathbf{r} \cdot \mathbf{R},
\]

which has been employed in several works for many-electron collision systems. The nuclear wave functions \(\chi_j\) are obtained by solving numerically the system of differential equations (8). From these solutions, the elements of the \(S\)-matrix are then calculated using standard collision theory, and the total cross section for the \(i \rightarrow j\) transition, \(\sigma_{ij}\), is given by

\[
\sigma_{ij} = \frac{\pi}{k_i^2} \sum_{l, j} (2J + 1) |S_{ij}^j|^2,
\]

where \(k_i\) is the initial linear momentum.

B. Semiclassical treatments

For impact energies above 1 keV, we employ the impact-parameter method (see e.g. [18]), where the nuclei follow straight-line trajectories with constant relative velocity \(\mathbf{v}\) and impact parameter \(\mathbf{b} (R = b + \mathbf{v})\), while the electronic motion is described by the wavefunction \(\Psi^{SC}(\mathbf{r}, \mathbf{t}; b, v)\), which is a solution of the equation

\[
\left( H_{\text{elec}} - i \frac{\partial}{\partial t} \right) \Psi^{SC}(\mathbf{r}, \mathbf{t}; b, v) = 0
\]

and is expanded as

\[
\Psi^{SC} = D(b, R) \sum_j a_j(b, v) \phi_j(\mathbf{r}, R) \exp \left[ -i \int_0^t \epsilon dt' \right],
\]

where \(D\) is a common translation factor (CTF) [19]:

\[
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\]
\[ D(r,R) = \exp \left[ \sum_{\alpha} f(r_{\alpha}, R) \left( v \cdot r_{\alpha} - \frac{1}{2} f^2(r_{\alpha}, R) v^2 t \right) \right]. \]

(15)

It has been shown [16,20] that the CTF method, with the same switching function, can be obtained from the CRC one by applying the eikonal approximation and assuming a constant and state independent local velocity. The coefficients of the expansion are solutions of the system of differential equations

\[ id_{ij} = \sum_{\ell} [v \cdot M_{ij} + v^2 B_{ij}] \delta_{ij} \exp \left[ -i \int_{0}^{t} (\epsilon_{ij} - \epsilon_{j}) dt' \right], \]

(16)

where \( M_{ij} \) has been defined in Eqs. (9) and (10) and \( B_{ij} \) are terms whose explicit form can be found in [19]. The radial and rotational components of the modified dynamical couplings are

\[ R_{ij} = \left\langle \psi_{j} \left| \frac{\partial}{\partial R} \right| \psi_{i} \right\rangle + A_{ij}^R \]

(17)

and

\[ L_{ij} = \left\langle \psi_{j} \left| \sum_{\alpha} i L_{\alpha}(r_{\alpha}) \right| \psi_{i} \right\rangle + A_{ij}^L, \]

(18)

where \( L_{ij} \) is the \( Y \) component of the electronic angular momentum operator.

The total cross section is given by

\[ \sigma_{ij}(v) = 2\pi \int_{0}^{\infty} b P_{ij}(b,v) db \]

(19)

where the probability \( P_{ij} \) for transition to the final state \( \psi_{j} \) is calculated from the coefficient \( a_{ij} \) of expansion (14):

\[ P_{ij}(b,v) = \lim_{t \to \infty} \left[ \langle \psi_{i} | \Psi \rangle - \delta_{ij} \right] = \lim_{t \to \infty} |a_{ij}(t;b,v) - \delta_{ij}|^2. \]

(20)

The quantal and semiclassical transition probabilities are related by [see Eqs. (12) and (19)]

\[ b P_{ij}(b) = \frac{(2J + 1)}{2k_i} |S_{ij}|^2 \]

(21)

with \( b = J/k_i \)

### III. MOLECULAR CALCULATIONS

The entrance channel of reaction (1) is a statistical mixture of singlet and triplet molecular states, while that of reaction (2) contains triplet and quintet states. Accordingly, we have calculated the electronic energies for states of the quasimolecule \( \text{NH}_2^+ \) with these multiplicities.

Molecular states \( \phi_i \) and energies \( \epsilon_i \) have been calculated using a multireference configuration interaction method (MRCI) with the program MELD [21]. This method starts with a SCF calculation in a basis of Gaussian type orbitals (GTOs); this provides a set of molecular orbitals (MOs) which are then used to construct the reference configurations. Each reference configuration is a symmetry- and spin-adapted linear combination of a few Slater determinants built up from products of the MOs. The configuration interaction (CI) space includes single and double excitations from the single Slater determinants.

\[ E_i = \sum_{\text{CI}} C_i^2 \langle \text{CI} | \Psi \rangle \]

\[ C_i = \langle \text{CI} | \phi_i \rangle \]

(22)

where the CI coefficients are given by

\[ C_i = \langle \text{CI} | \phi_i \rangle \]

(23)

The calculation of the CI coefficients is a complex problem, and various methods have been proposed to solve it. One of the most widely used methods is the configuration interaction singles (CIS) method, which is based on the approximation that the CI coefficients are proportional to the overlap between the reference configuration and the excited state.

\[ C_i = \langle \text{CI} | \phi_i \rangle \]

(24)

where \( \phi_i \) is the excited state wave function and \( \langle \text{CI} | \phi_i \rangle \) is the overlap between the reference configuration and the excited state wave function.

The CI coefficients are used to construct the excited state wave function, which is a linear combination of all the CI coefficients.

\[ \Psi = \sum_{\text{CI}} C_i \phi_i \]

(25)

where \( \phi_i \) is the excited state wave function and \( C_i \) is the CI coefficient.

The electronic energy of the excited state is then given by

\[ E_i = \sum_{\text{CI}} C_i^2 \langle \text{CI} | \Psi \rangle \]

(26)

where the CI coefficients are given by

\[ C_i = \langle \text{CI} | \phi_i \rangle \]

(27)

where \( \phi_i \) is the excited state wave function and \( \langle \text{CI} | \phi_i \rangle \) is the overlap between the reference configuration and the excited state wave function.

The CI coefficients are used to construct the excited state wave function, which is a linear combination of all the CI coefficients.

\[ \Psi = \sum_{\text{CI}} C_i \phi_i \]

(28)

where \( \phi_i \) is the excited state wave function and \( C_i \) is the CI coefficient.
occupied. (ii) Doubly excited configurations are selected using second order perturbation theory: for each subsystem, only those configurations with a contribution larger than $5 \times 10^{-6}$ Hartree to the energy of any of the lowest \(n\)th-order wave functions were kept. We have taken the zeroth-order wave functions as the eigenvectors of the Hamiltonian matrix in the basis of reference configurations, with \(n=16\) for \(\Psi^0\) and \(\Psi^0\) systems, 14 for \(\Psi^1\), 10 for \(\Psi^2\), 7 for \(\Psi^3\) and 9 for \(\Psi^4\) subsystems, respectively.

The set of reference configurations was allowed to change iteratively at each \(R\) in the following way: For each of the six subsystems, an initial guess of 80 reference configurations was generated in the limit \(R \rightarrow \infty\); this set contained the basic structures of the atomic channels to be included in the dynamical calculation (those listed in Table I). Using this set we carried out a MRCI calculation, and we selected the 80 configurations with the largest contributions to the lowest 16 \(\Psi^0\) and \(\Psi^1\) states, 14 \(\Psi^2\), 10 \(\Psi^3\), 7 \(\Psi^4\), and 9 \(\Psi^5\) states obtained in this calculation, which were then used as a new reference set, and the selection procedure was repeated. After three iterations the reference set converged and the weight of the reference configurations in the calculated CI functions was larger than 96\% for the states of Table I. To ensure a similar precision of the wave functions at any internuclear distance, the selection of the reference set was repeated at each value of \(R\), with the converged reference set at a given value of the internuclear distance \(R_i\) used as the initial guess at a nearby point \(R_{i+1}\) \((R_i>R_{i+1})\). In practice, \(R_i-R_{i+1}=0.2a_0\) a except for \(R<4a_0\) and in the regions of avoided crossings, where the step size was reduced to 0.05\(a_0\). The CI space included up to \(3.2\times10^5\) Slater determinants for \(\Psi^0\), \(3.1\times10^5\) for \(\Psi^1\), \(1.1\times10^5\) for \(\Psi^2\), \(1.6\times10^5\) for \(\Psi^3\), \(1.6\times10^5\) for \(\Psi^4\), and \(1.7\times10^5\) for \(\Psi^5\).

As a check of the accuracy of our calculation, we compare in Table I the calculated atomic energies [singlets and triplets relative to the ground state of \(N^2+\) and quintets relative to the metastable \(N^2+(4P)\)] of the \(N^+\) and \(N^2+\) states included in the dynamical calculation with the experimental values [22]. The errors in these energy differences are smaller than 0.3 eV for the relevant channels and the error in the ionization potential of \(H(1s)\) is smaller than \(3 \times 10^{-3}\) eV; this is sufficient for the dynamical calculation. We also include in this table the symmetries of the states of the \(NH^2+\) quasimolecule correlating to each atomic state. Molecular states and their asymptotic atomic limit will be referred in the text according to the labels of the first column of the table.

The energies of triplet, singlet, and quintet molecular states are depicted in Figs. 1–3, respectively. In the triplet subsystem, the energies of the molecular states \(1\Sigma^+\) and \(1\Pi\), which are the entrance channels of reaction (1), show avoided crossings with those molecular states of the same symmetry correlating to channel 9 at about \(R=12a_0\) and with those of channel 8 at about \(R=6.5a_0\). The first ones are very narrow and have been crossed diabatically. In the singlet subsystem (Fig. 2) the energies of the entrance channels \((1\Sigma^+, 1\Pi)\) do not show narrow avoided crossings with those of the EC channels, and the most likely mechanism for EC in this subsystem involves \(1\Pi\)–\(1\Pi\) transitions in the wide avoided crossing at \(R=2a_0\).
FIG. 3. Potential energy curves of (NH)\(^{2+}\): quintet subsystem. Channels are labeled according to Table I.

The dynamical couplings of equations (17) and (18) were evaluated numerically, as explained in [24]; this method involves the calculation of the delayed overlap matrix elements \(\langle \phi_i(R) | \phi_f(R+\delta) \rangle\). In this work we have used \(|\delta|=10^{-4}a_0\). An important practical difficulty in applying the molecular expansion to many-electron systems is the erratic sign of the molecular wave functions \(\phi_i\), which results in meaningless signs of the dynamical couplings. To solve this arbitrariness, we have implemented an algorithm to automatize the sign coherence of the molecular states \(\phi_i\), both between successive grid points \((R_j, R_{j+1})\) and in the calculation of the couplings \((R_j, R_{j+1})\). This method is based on the evaluation of the delayed overlaps \(\langle \phi_i(R) | \phi_f(R+\delta) \rangle\) and \(\langle \phi_i(R_j) | \phi_f(R_{j+1}) \rangle\) and will be published elsewhere [25].

As an illustration, we have plotted in Figs. 4(a) and 4(b) the most important modified radial couplings [see Eq. (17)] and in Figs. 4(c) and 4(d) some rotational ones [Eq. (18)]. The main mechanism of reaction (1) at low energy involves transitions between \(1^3\Pi\) and \(8^3\Pi\) in the neighborhood of \(R\approx 6.5a_0\) and \(3.25a_0\) [see the avoided crossings in Fig. 1 and the two peaks in the corresponding coupling in Fig. 4(a)]. and \(1\rightarrow9^2\Sigma^+\) and \(1\rightarrow9^1\Pi\) avoided crossings at \(R\approx 2.25a_0\) in Fig. 1 [see the single peaks of the corresponding couplings in Fig. 4(a)]. These transitions are strongly affected by \(1\,^5\Sigma^+\rightarrow8^3\Pi\) rotational couplings, Fig. 4(c). For reaction (2), the mechanism at low energy involves transitions between states \(2^3\Sigma^-\rightarrow13^3\Sigma^-\) at \(R\approx 8.1a_0\) and \(2^3\Pi\rightarrow11^3\Pi\) at \(R\approx 6.1a_0\) [see the radial couplings in Fig. 4(b) and rotational ones in Fig. 4(d)].

IV. DYNAMICAL RESULTS

A. Total EC cross section in N\(^2\)\((2s^22p\,^2p^o)\)+H(1s) collisions

We have calculated the total cross sections for the EC reaction (1) by employing a 56-term molecular basis set; this basis includes the triplet and singlet states whose energies are plotted in Figs. 1 and 2, respectively. The above mentioned cross section is obtained as

\[
\sigma = \frac{1}{12}\left[\sigma(1\,^1\Sigma^+) + \sigma(1\,^1\Pi_u) + \sigma(1\,^1\Pi_d)\right] + \frac{3}{12}\left[\sigma(1\,^3\Sigma^+) + \sigma(1\,^3\Pi_u) + \sigma(1\,^3\Pi_d)\right],
\]

where \(\sigma(i)\) are the cross sections obtained for the capture reaction with initial channel \(i\). Our cross sections (tabulated values are available at [27]) are compared in Fig. 5 with experimental results and previous theoretical values. We have restricted the energy range to \(E<300\text{ keV}\), where ion-

FIG. 4. Selected radial and rotational couplings between terms of different channels in the triplet subsystem, as indicated in the panels.

FIG. 5. Total EC cross sections in N\(^2\)\((2s^22p\,^2p^o)\)+H(1s) collisions [reaction (1)]. Present calculations, — semiclassical calculation; — quantum calculation. Experimental results, □ [3]; ♦ [4]; ▲ [5]; ○ [6]. Theoretical results, ——— [8]; ——— [9].
The low-energy mechanism, as already explained by Herrero et al. [9], is the transition in the avoided crossings between the molecular states dissociating into channels 1 and 8 at $R = 6.4a_0$ (Fig. 1, bottom left panel); this mechanism is illustrated in Fig. 6(a), which shows the Stueckelberg oscillations, typical of the Landau-Zener model. To check the contribution of transitions in the 1-9 avoided crossing, we have carried out a 6-state $\{1 3\Sigma^+, 1 3\Pi_5^-, 9 3\Sigma^+, 9 3\Pi_7^+\}$ calculation with the dynamical couplings evaluated at closely spaced points in the avoided crossing region; this test yields values smaller than 0.11 $\hat{A}^2$ at the lowest energies considered in our calculation and, accordingly, it has been traversed diabatically. In practice, we have fitted the sharp peaks of the 1-9 radial couplings to Lorentzian functions, which have been subtracted from the calculated radial couplings, while the corresponding interaction matrix elements have been retained in the quantal calculation. This procedure also allows us to check the influence of the accuracy of our molecular data in the cross section by shifting the energy of the entrance channel to match the experimental asymptotic 1-9 energy difference. The two-state calculations with these shifted energies $(1 3\Sigma^+ - 9 3\Sigma^+ \text{ and } 1 3\Pi - 9 3\Pi)$ yield cross sections smaller than 0.30 $\hat{A}^2$, remaining negligible compared to those produced by the 1-8 transitions.

In Fig. 5, we see that our results are systematically higher than those of the calculation of Herrero et al. [9]. To understand the reason for this, we have plotted in Fig. 7 the contribution of the triplet states to the total EC cross section, which shows that the contribution of the singlet states is negligible at $E < 400$ eV, and that the cross section of Ref. [9] agrees with our triplet contribution at $E > 600$ eV. Therefore, the difference between the two calculations is not a consequence of the approximation of Ref. [9] of neglecting the contribution of singlet states and must be due to small differences in the molecular wave functions, which become relevant at low impact energies. For instance, fitting the energies of states 1 3H and 8 3H near their pseudocrossing, we obtain the following Landau-Zener parameters (see [18] and references therein): $R_0 = 6.439a_0$ (crossing point), $a = 0.0256$ hartrees/$a_0$ (difference of slopes), and $H_{12} = 0.0018$ hartrees.

**FIG. 6.** $bP(b)$ as a function of $b$ for EC in reaction (1) at three energies (labeled in the panels) showing three different mechanisms.

**FIG. 7.** Total cross sections for reactions (1) and (2), as indicated in the figure. The contributions of the triplet states to the total cross sections for reaction (1) and the results of Ref. [9] are also included. For $E < 1$ keV, the cross sections have been calculated using the quantal treatment and the semiclassical one for $E > 1$ keV (interaction), while those of Ref. [9] are $R_0 = 6.546a_0$, $a = 0.026$ hartrees/$a_0$, and $H_{12} = 0.00145$ hartrees. We have checked that the small difference in the value of $H_{12}$ leads to an approximate factor of 1.3 in the cross section, in agreement with the results of the full calculation shown in Fig. 5. Since our energies are slightly lower than those of Ref. [9], and show better agreement with the spectroscopic atomic levels, we conclude that our calculation is more precise at low impact energies. As in Ref. [9], we obtain a maximum of the total cross section at $E = 4$ eV, which is not found in the merged-beam experiments [6].

At $E = 2$ keV, our total cross section shows a local maximum, while the maximum of the experimental data of Wilkie et al. [5] is shifted to $E = 5$ keV, and agrees with the two-state calculation of Bienstock et al. [8]. On the other hand, for $E < 20$ keV, our cross section lies parallel to and is about 25% higher than that of Piekema et al. [6]. In this energy range, the avoided crossings of the entrance channel at $R \approx 6.4a_0$ are traversed diabatically, and the most important transitions take place near the avoided crossings at $R \approx 3.25a_0$ and $R \approx 2.25a_0$ to channels 8 and 9, respectively (see the peaks in the radial couplings of Fig. 4(a)); this is illustrated in Fig. 6(b) for $E = 1.7$ keV.

To check our calculation in this energy region, we have studied the convergence of the molecular expansion. In Fig. 8(a) we compare the EC transition probabilities calculated with a (minimal) two-state basis $\{1 3\Pi_6, 8 3\Pi_7\}$, similar to that used in [8], an eight-state basis $\{1 3\Sigma^+, 1 3\Pi_5^-, 8 3\Sigma^-, 8 3\Pi_6^+, 8 3\Pi_6^-, 8 3\Delta_5^+\}$ that includes all the states of channels 1 and 8, with their radial and rotational couplings, and the whole basis (35 states) of the triplet subsystem. We can observe in this figure that, for $3.5 < b < 5a_0$, there is an important difference between the transition probabilities, and hence in the corresponding cross section, of the two-state and the eight-state calculations, which is mainly due to the influence of the rotational couplings of Fig. 4(c). A small change is found, however, on increasing the basis to 35 states. These results point
out that the calculations for the total EC cross section and, in particular, for the cross section for formation of \(N^+(2s^2p^2^3P^0)\) (channel 8) are correctly described with our basis, while the two-state calculation is not converged. Therefore, the good agreement between the experiment of Wilkie et al. [5] and the two-state model of Bienenstock et al. [8] should be taken as fortuitous.

With respect to the validity of the semiclassical treatment at this intermediate energy region, we have found that quantal and semiclassical cross sections, as shown in Fig. 5, and transition probabilities, are practically identical for \(E > 1\) keV. At lower energies, there are sizable differences between the two calculations; this is illustrated in Fig. 8(b), where we plot the values of \(bP(b)\) vs \(b\) for the EC process with entrance channel 1\(^3\)IL at \(E = 560\) eV. We see in Fig. 8(b) a shift of the maxima of the transition probabilities, which was also found in a similar comparison for EC in Be\(^{1+}\)+H collisions [16].

Finally, for energies between 5 and 300 keV, Fig. 5 shows that our results are in very good agreement with the measurements of Refs. [3–5]. At high energies (\(E > 20\) keV), triplet states dissociating into channels 5 and 11 and singlet states dissociating into channels 6, 7, 10, and 12 become accessible. This leads to the two-peak structure of the transition probabilities shown in Fig. 6(c): the outer peak, in both the singlet and triplet subsystems, is produced by transitions to higher (in energy) channels (11, 10, and 12) while transitions to lower (in energy) channels (5, 6, and 7) produce the inner peak.

**FIG. 8.** \(bP(b)\) for EC in \(N^+(2s^2p^2^3P^0)+H(1s)\) collisions. (a) Contribution of the triplet subsystem for \(E = 1.26\) keV, calculated with 2-, 8-, and 35-state molecular basis sets, as indicated in the figure. (b) \(bP(b)\) for EC at \(E = 560\) eV. Lines are labeled in the figure: SC stands for the semiclassical calculation and QM stands for the quantal one.

Since merged-beam experiments are carried out using a D target, while the results shown in Fig. 5 considered collisions with H, it is useful to study the isotopic dependence of the cross sections. To illustrate this effect, we compare in Fig. 9 the EC total cross section from H and D, which shows a significant isotopic effect only for \(E < 10\) eV, but the maximum at low impact energies is obtained for both targets. One can also note in this figure a small, but nevertheless surprising, isotopic dependence in the region 100 < \(E < 500\) eV. To explain this unexpected effect, we have compared in Fig. 10 the transition probabilities for EC in collisions with both isotopic species at \(E = 35\) and 140 eV. As we have already mentioned, at \(E < 100\) eV, the dominant mechanism involves transitions in the pseudocrossing region at \(R = 6.4a_0\). At \(E > 100\) eV, transitions at \(R = 3.0a_0\) start to be noticeable. Leading to the peaks at \(b < 3.0a_0\) (see Fig. 10, \(E = 140\) eV). Since trajectory effects, which depend on the nuclear masses, are more important for trajectories with small \(b\), this explains the apparent paradox of more important isotopic dependence at relatively higher energies.

**C. Total EC cross section in \(N^+(2s^2p^2^3P^0)+H(1s)\) collisions**

Total cross sections for reaction (2) are obtained with the relation

\[
bP(b) \propto \frac{1}{b^2} \sum_{j=1}^{J} \left| \langle n_2, l_2 | \mathbf{P} | n_1, l_1 \rangle \right|^2 \delta(E - E_{n_1, l_1, j})
\]

**FIG. 9.** Comparison of EC total cross sections in collisions \(N^+(2s^2p^2^3P^0)+H(1s)\) and \(D(1s)\), as indicated in the figure. ●, experimental results of [6] for \(N^+(2s^2p^2^3P^0)\) collisions with D.

**B. Isotopic dependence**

**FIG. 10.** \(bP(b)\) as a function of \(b\) [see Eq. (21)] for electron capture in collisions \(N^+(2s^2p^2^3P^0)+H(1s)\) and \(N^+(2s^2p^2^3P^0)\) +D(1s), at the impact energies indicated in the figure.
In this respect, the good agreement of our total cross section would be more easily noticed in the total cross section of metastable $\text{N}_2^+$ ions in the corresponding initial stable ions is required to get good agreement with the experimental results.

In the bottom panel, we plot the total EC cross sections in the same energy range. In this panel the theoretical results are --- cross section for reaction (1); -- cross section for reaction (2); — cross section obtained for a beam containing 40% of metastable $\text{N}_2^+(2s2p^2P^o)$ and 60% of ground state $\text{N}_2^+(2s2p^2P^o)$ ions. Experimental results □ [3]; ◇ [4]; ▲ [5]; ■ [2]; ● [6].

\[
\sigma = \frac{1}{8} \left[ \sigma(2^3\Sigma^-) + \sigma(2^3\Pi_u) + \sigma(2^3\Pi_l) \right] + \frac{5}{24} \left[ \sigma(2^5\Sigma^-) + \sigma(2^5\Pi_u) + \sigma(2^5\Pi_l) \right],
\]

where the notation is similar to that of Eq. (22). We have employed in this calculation the set of 35 triplet states also used for reaction (1), and 15 quintet molecular states. The ensuing cross sections are plotted in Fig. 7. At $E<0.1$ keV and $E>30$ keV, the cross sections for reactions (1) and (2) show similar values and energy dependences, indicating that a contamination of the initial beam by metastable ions would be unnoticeable by comparing experimental and theoretical total EC cross sections. On the contrary, for $0.1<E<30$ keV, the presence of metastable ions in the experiment would be more easily noticed in the total cross section. In this respect, the good agreement of our total cross section for reaction (1) with the experiments of Refs. [3–5] for $E>5$ keV indicates that there was a very small proportion of metastable $\text{N}_2^+$ ions in the corresponding initial beams. On the other hand, the disagreement of the cross section measured in [6] with other data in the region $0.1<E<30$ keV might be attributed to a larger proportion of metastable ions in that experiment. However, as shown in the bottom panel of Fig. 11, a proportion of 40% of metastable ions is required to get good agreement with the experimental results of Piekema et al. [6], who did not find any evidence of such a high proportion of metastable ions. Nevertheless, we can observe good agreement between all experiments and our calculation for $E>30$ keV, where the cross sections for reactions (1) and (2) are very similar. On the other hand, the shift of the maximum ($E\approx2$ keV) of the cross section in our calculation with respect to that of the experiment of Wilkie et al. ($E=5$ keV) (see Fig. 11) cannot be related to the possible presence of metastable ions.

**D. State-selective EC cross sections**

We compare in Fig. 11 the partial cross sections for populating states $8^3D$ and $9^3P^o$ through reaction (1) with the experimental values of [5,2]. We also include the partial cross sections for populating $11^3P^o$ and $15^3D$ channels with reaction (2) because they would produce peaks overlapping with the previous ones in the energy change spectrum.

Although we find a reasonable agreement, a shift, similar to that found for the total cross section (see also the bottom panel of Fig. 11), can be noticed in this figure, which is not surprising given that the experimental total cross section was used to obtain the partial ones in those works. Cross sections for several exit channels and in an extended energy range are presented in Fig. 12, where we plot the contribution ratio of the individual channels, calculated as

\[
\chi_i = \frac{\sigma_i}{\sum_j \sigma_j} \times 100,
\]

with $i$ and $j$ running over the EC channel index.

The relative values of the partial cross sections of Fig. 12 for reaction (1) can be qualitatively explained by taking into account only transitions from the entrance channels. As we have already discussed, reaction (1) takes place through tran-
sitions to states of channel 8. At high \( v \), other triplet states (channels 5 and 11) are populated. In the case of reaction (2) and at low \( v \), the dominant exit channels (11 \( ^3P^o \) and 13 \( ^3S^o \)) are populated in the avoided crossings at \( R \approx 6.1 a_0 \) and \( 8.1a_0 \), respectively. The ratios of Fig. 12 are due to the initial statistical mixture: the states correlating with 11 \( ^3P^o \) are populated in the avoided crossing at \( R \approx 6.1 a_0 \), which appears in the \( ^3 \Pi \) subsystem, whose statistical weight is 2/8, while the state correlating with 13 \( ^3S^o \) is populated in the avoided crossing at \( R \approx 8.1 a_0 \) in the \( ^3 \Sigma^- \) subsystem, with a statistical weight of 1/8. At \( E > 1 \text{ keV} \), the avoided crossings at large \( R \) are traversed diabatically, and the main transitions take place at \( R \approx 3a_0 \) via the maximum of the 2 \( ^3 \Sigma^- - 13 \ ^3 \Sigma^- \) coupling (see Fig. 4), which leads to a dominant population of the channel 13 \( ^3S^o \). As in the case of reaction (1), for energies above 10 \text{ keV}, other channels (9 \( ^3P^o \), 8 \( ^3D^o \), 20 \( ^3P \), 21 \( ^3D^o \) become accessible).

V. CONCLUSIONS

We have calculated state-selected EC cross sections in collisions of \( \text{N}_2^+ \) in ground \( (2s^22p^2 \ ^1P^o) \) and metastable \( (2s^22p^2 \ ^3P^o) \) states with H(1s) and D(1s), by employing a molecular expansion with \textit{ab initio} molecular wavefunctions, and quantal and semiclassical treatments. The use of the quantal approach has allowed us to gauge the isotopic dependence of the cross section and the accuracy of the semiclassical eikonal approach. Our calculations yield very similar cross sections for reactions (1) and (2) with the exception of the energy region 0.2–30 \text{ keV}, where the comparison of our results with the values of Refs. [4,5] does not show a noticeable contamination by metastable ions in those experiments.

At low \( E(E<1 \text{ keV}) \), we have reproduced the energy dependence and the maximum at \( E \approx 4 \text{ eV} \) of the calculation of [9] for reaction (1). One result of our calculation is the branching ratios for populating different EC channels. We have found that the EC from \( \text{N}_2^+(2s^22p \ ^3P^o) \), and at energies lower than 40 \text{ keV}, involves the simultaneous excitation of one projectile electron, leading to \( \text{N}^+(2s2p \ ^3D^o)+\text{H}^+ \). Several collision channels are formed at higher energies. In the collision of metastable \( \text{N}_2^+(2s2p \ ^3P^o) \), the dominant EC channels are, at low energies, \( \text{N}^+(2s2p3s \ ^3P^o)+\text{H}^+ \) and \( \text{N}^+(2s2p \ ^3S^o)+\text{H}^+ \).

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