Electron capture in collisions of N^{2+} and O^{2+} ions with H(1*s*) at low impact energies

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(Received 20 July 2005; published 10 August 2006)

We present *ab initio* quantal calculations of electron capture cross sections for collisions of ground and metastable states of $^{14}N^{2+}$ and $^{16}O^{2+}$ ions with H(1*s*), at collision energies $10^{-2} < E < 10^{2}$ eV/amu. The calculation for N^{2+}+H updates the previous one of Barragán *et al.* [Phys. Rev. A **70**, 022707 (2004)] at $0.1 < E < 0.3$ eV/amu. Total cross sections for both systems show large values of about 5×10^{-15} cm^2 at $E < 0.1$ eV/amu, where they exhibit resonant structures.

DOI: 10.1103/PhysRevA.74.024701 PACS number(s): 34.70.+e, 34.10.+x

Electron capture (EC) in collisions of O^{2+} and N^{2+} ions with H are important processes in astrophysical (see Ref. [1], and references therein) and fusion plasmas [2]. Since low impact energies are needed in these applications, we have extended to lower energies the semiclassical calculation of Ref. [3] for the EC reactions

$$O^{2+}(2s^2 2p^2\ ^3P) + H(1s) \rightarrow O^+ + H^+, \quad (1)$$

$$O^{2+}(2s^2 2p^2\ ^1D) + H(1s) \rightarrow O^+ + H^+, \quad (2)$$

$$O^{2+}(2s^2 2p^2\ ^1S) + H(1s) \rightarrow O^+ + H^+, \quad (3)$$

and we have recalculated and extended to lower energies the cross sections for reactions

$$N^{2+}(2s^2 2p\ ^2P^o) + H(1s) \rightarrow N^+ + H^+, \quad (4)$$

$$N^{2+}(2s2p^2\ ^4P) + H(1s) \rightarrow N^+ + H^+ \quad (5)$$

previously evaluated in Ref. [4]. In the present work we study the shape of these cross sections at low energies, the presence of resonant structures and we discuss the limitations of previous calculations.

The calculation of EC cross sections at low energies requires the use of a quantal treatment for the dynamics, including reaction coordinates (see Ref. [5], and references therein), to ensure that the expansion fulfills the collision boundary conditions. In the present work we have defined the reaction coordinate in terms of the switching function of Ref. [6].

We have evaluated the molecular wavefunctions by applying a multireference configuration interaction (CI) treatment by means of the program MELD [7]. In this method, one constructs a basis of configurations by allowing single and double excitations from a set of reference configurations; these are antisymmetrized products of SCF molecular orbitals, which are linear combinations of Gaussian type orbitals. The Gaussian basis and the set of reference configurations have been chosen (details can be found in Refs. [3,4]) in order to ensure that the asymptotic energy differences differ in less than 0.2 eV from the spectroscopic values [28] for all the states involved. The dynamical couplings have been evaluated as explained in Ref. [8].

In O^{2+}+H collisions we have employed an expansion in terms of 29 molecular states. Since the entrance channel of reaction (1), $O^{2+}(2s^2 2p^2\ ^3P)$+H(1*s*), correlates to molecular states $^{2,4}\Sigma^-$ and $^{2,4}\Pi$, doublet and quadruplet molecular states are involved in reaction (1), with statistical weights 1/3 and 2/3, respectively. As it has been explained in previous works [3,9,10], reaction (1) takes place mainly through transitions to the states $^4\Sigma^-$, $^4\Pi$, dissociating into $O^+(2s2p^4\ ^4P)$+H^+, in the avoided crossings between the corresponding potential energy curves at $R \simeq 4$ and $4.5a_0$, respectively. Reactions (2) and (3) take place through transitions between doublet molecular states.

To ensure the validity of our molecular treatment at low impact energies, we have recalculated the potential energy curves of the quadruplet states by employing the [4*s*3*p*2*d*1*f*] Gaussian basis set centered at the O nucleus of Ref. [11], and reducing the perturbative selection threshold to 5×10^{-7} hartree, This leads to an asymptotic energy difference between the channels O^{2+} $(2s^2 2p^2\ ^3P)$ and O^+ $(2s2p^4\ ^4P)$ that differs in less than 0.18 eV from the experimental value. We have selected iteratively the reference space at each internuclear distance, which yields a total CI space of about 70 000 configurations at $R < 2.0a_0$.

The total cross section for reaction (1) is shown in Fig. 1, where we have included the semiclassical results of Ref. [3] to illustrate the smooth joining of both calculations. To discard the possibility of spurious maxima at large *R*, we have also checked that the cross section of Fig. 1 does not vary when the numerical entrance channel potentials are substituted at $R > 12a_0$ by polarization-type expressions $c_1 - c_2 R^{-4}$. For $E < 0.2$ eV/amu, the energy dependence of the EC cross can be approximately described by the Langevin model (see Refs. [16,17]) and some spikes are noticeable, most of them due to shape resonances in the adiabatic entrance channel potential, as also found in the calculations of Refs. [15,18]. To further illustrate these resonances, we show in Fig. 2 the values of $\sigma(^4\Pi_+)$, which is the contribution to the EC cross section of the EC reaction with entrance channel the molecular state $^4\Pi_+$; this state dissociates into O^{2+} $(2s^2 2p^2\ ^3P)$ +H(1*s*), and the corresponding electronic wave functions is symmetric under reflection in the collision plane (subindex +). In this figure we have added the values of the vibroro-

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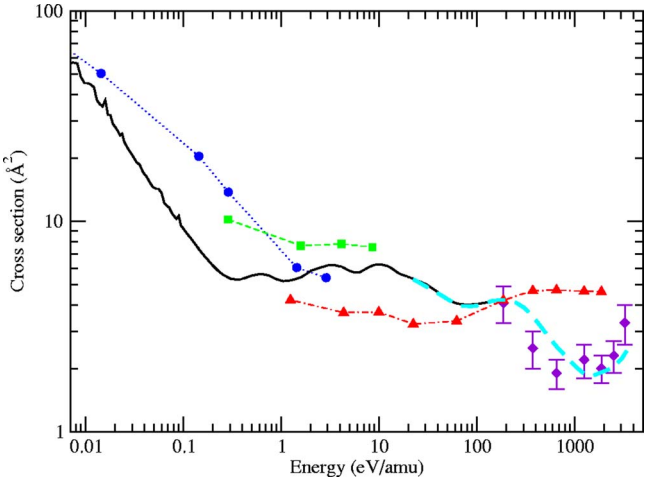

FIG. 1. (Color online) Total EC cross sections in $O^{2+}(2s^2 2p^2\ ^3P)+H(1s)$ collisions. Full line, present results; dashed line, semiclassical results of Ref. [3], ■, quantal calculation of Ref. [12]; ●, quantal calculation of Ref. [10]; ▲, semiclassical results of Ref. [13]; ♦, experimental results of Ref. [14].

tational quantum numbers (v,j) of the shape resonances; these have been obtained analyzing the contribution of each j-partial wave to the total cross section and with the help of the program LEVEL 7.7 [19]. As the energy decreases, the positions of the resonances in the cross section show significant shifts with respect to the energies of the quasibound states calculated with LEVEL 7.7, probably due to the interaction of the entrance channel with the capture channel dissociating into $O^+(2s2p^4\ ^4P)$. In this respect, an indication of the importance of the nonadiabatic interaction is given by the peak at $E \simeq 0.013$ eV/amu. To assign this peak, we have obtained a set of diabatic states by means of an unitary transformation that cancels out the radial coupling between the molecular states of the basis set, Solving the radial Schrödinger equation with the diabatic potential of the entrance channel allows us to assign the peak to the (5,19) quasibound state of this potential.

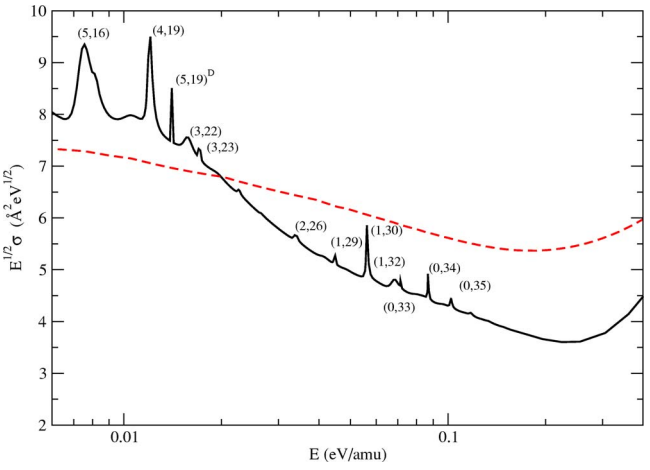

FIG. 2. (Color online) Contribution $\sigma(^4\Pi_+)$ of the $^4\Pi_+$ subsystem to the cross section for reaction (1). The labels (v,j) in the peaks are the vibrorotational quantum numbers of the resonant states of the adiabatic potential of the molecular entrance channel, with the exception of the resonance labeled with the superscript D, which corresponds to a quasibound state of the diabatic entrance channel. The dashed line is the result of applying a two-state semiclassical model (see text).

The calculated EC cross section is smaller than that given by the Langevin model (it yields a constant value $\sigma\sqrt{E} \approx 18.8$ Å^2 eV$^{1/2}$ in Fig. 2), because the transition probability is smaller than 1, as assumed in that model for collisions with $b < b_{max} = (2\alpha q^2/\mathcal{E})^{1/4}$, where α is the H$(1s)$ polarizability and $\mathcal{E}$ is the center-of-mass energy. To illustrate this, we have calculated the cross section $\sigma(^4\Pi_+)$ by applying a simple model where the transition probability is estimated by using the Landau-Zener model. This yields (see, e.g., Ref. [20]):

$$\sigma = 2\pi \int_0^{b_{max}} bP(b)db \approx 2\pi \int_0^{b_{max}} b2p(1-p)db \qquad (6)$$

with $p=\exp[-2\pi H_{12}^2/av_R]$, where H_{12} is the interaction, $a = d(H_{22}-H_{11})/dR$, and v_R is the radial velocity in the crossing point $R=R_0$, which has been calculated by employing the numerical value of the adiabatic entrance channel potential. The reasonable agreement of this model with the numerical values (Fig. 2) indicates that the cross section is determined by b_{max} and the transition probability in the crossing region. In addition, as in Ref. [17], the energy dependence of the Landau-Zener probability qualitatively explains the relatively small deviation of the EC cross section from the $E^{-1/2}$ behavior.

At collision energies $0.5 < E < 10$ eV/amu, the cross section for reaction (1) shows an oscillatory structure as a function of the energy, caused by an interference effect between transitions in two avoided crossings at $R \simeq 2.5$ and $4.0a_0$ in the $^4\Pi$ subsystem. The differences between our cross sections and the previous ones of Refs. [13,10] are due to the more precise molecular wavefunctions employed in the present work, as pointed out in [3].

The calculations for $N^{2+}+H$ collisions (Figs. 3 and 4) have employed the 56-term basis set previously used in the quantal calculation of Ref. [4], with the only difference of a finer grid of internuclear distances, as explained below. The mechanisms of reactions (4) and (5) have been discussed in detail by Barragán *et al.*[4]. Reaction (4) involves singlet and triplet molecular states (statistical weights 1/4 and 3/4), and at low energies, it takes place through transitions in the avoided crossing between the triplet states dissociating into $N^{2+}(2s^2 2p\ ^2P^o)+H(1s)$ and $N^+(2s2p^3\ ^3D^o)+H^+$. Triplet and quintet molecular states are required to evaluate the cross section for reaction (5), where the main mechanism involves transitions from the molecular entrance channels to states correlating to $N^+(2s^2 2p3s\ ^3P^o)+H^+$ and $N^+(2s2p^3\ ^3S^o)+H^+$. As in $O^{2+}+H$ collisions, the cross sections for both reactions reach similar values at low impact energies and show resonant structures (see Figs. 3 and 4).

For $E > 0.2$ eV/amu, the present results agree with the previous ones of Ref. [4] and, in particular, the cross section for reaction (4) agrees with the semiclassical result. To further illustrate the comparison of our cross sections with the

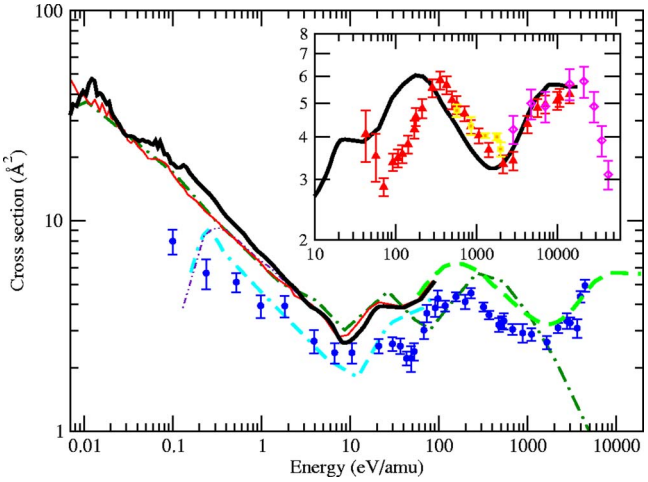

FIG. 3. (Color online) Total EC cross sections in $N^{2+}(2s^2 2p\ ^2P^o)+H(1s)$ collisions. Solid lines, present calculation: Thick line, results for collisions with H, thin line, results for collisions with *D*. Experimental results: □, [14]; ◇, [21]; ▲, [22]; ●, [23]. Previous theoretical results: ·–·–, [24]; ·–·–·, [25]; –··–, quantal calculation of Ref. [4]; ---, semiclassical calculation of Ref. [4].

available experimental results, they are shown in the inset of Fig. 3 for $E>10$ eV. However, at $E<0.2$ eV/amu, the cross sections reported in our previous work decrease rapidly and this behavior disappears in the new calculation that uses a finer grid of internuclear distances. We have found that in the previous work, the diabatic potential of the entrance channel, obtained after interpolation and integration of the radial couplings, showed a small spurious maximum of about 0.1 eV at large *R*, which gave rise to the rapid decrease of the cross section. A similar difficulty could explain the corresponding

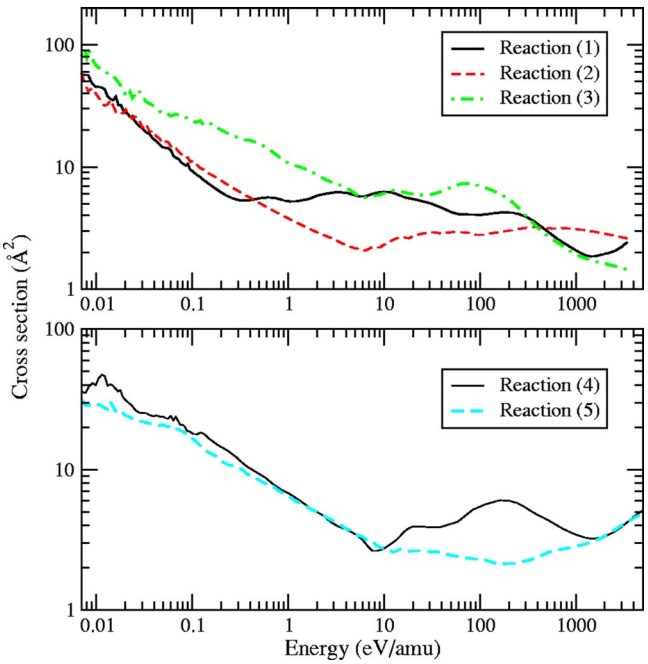

FIG. 4. (Color online) Total cross sections for EC processes for ground state ions [reactions (1) and (4)], and metastable ions [reactions (2), (3), and (5)].

maximum in the calculation of Ref. [25]. In this work we have checked our calculation, as explained above for $O^{2+}+H$ collisions to ensure that our new results do not present this limitation in the energy range of Fig. 3.

Our cross section for reaction (4) and those from previous calculations [24,25] show a Langevin-type behavior $\sigma \sim E^{-1/2}$ at low energies. As explained in Ref. [4], the differences between the theoretical results are mainly due to the accuracy of the gap between the energies of the entrance molecular channel and that dissociating into $N^+(2s2p^3\ ^3D^2)$. In particular, the change of this gap from 0.079 eV [25] to 0.099 eV [4] leads to an increase of the capture cross section by a factor of 1.3 at $E\approx 1$ eV/amu. Given the sensitivity of the cross section to the accuracy of the molecular data, we have checked our calculation by enlarging the Gaussian basis set of Ref. [4]. We have also reduced the selection threshold in the CI step to 7×10^{-8} hartree, which leads to a CI space that includes about 85 000 configurations in the avoided crossing region $R\approx 6.5a_0$. A test on the accuracy of our calculation is provided by the comparison between the electronic gradient matrix elements calculated numerically and by applying the relationship

$$\langle i|\nabla|j\rangle = (E_j - E_i)\langle i|\boldsymbol{r}|j\rangle, \tag{7}$$

which is fulfilled by exact eigenfunctions of the electronic Hamiltonian. Our values for the *Z* component of the electronic gradient (the only nonvanishing) between the $^3\Pi$ wave functions of the entrance and the main exit channels are $0.0110a_0^{-1}$ (numerical) and $0.0109[a_0^{-1}]$ [from Eq. (7)] at $R=6.4a_0$. Although the enlargement of the basis set yields energy decreases of about 8×10^{-2} eV in the avoided crossing region, the energy gap changes in less than 3×10^{-3} eV. In order to estimate the error in the EC cross sections associated to these changes in the energy gap, we have employed the Landau-Zener model that leads to variations of the cross section smaller than 10%.

The merged-beams experiment of Ref. [23] reported a cross section smaller than the theoretical ones, and, in contrast to results for other collisions, the absolute value of the slope of the logarithmic $\sigma-E$ plot (Fig. 3) is smaller than the Langevin value 0.5 at $E<2$ eV/amu. In order to compare with these experimental values, we have evaluated the EC cross section for the reaction with deuterium, which is slightly lower than that with H (see also Refs. [16,26,27]). The ratio σ_H/σ_D is smaller than 1.2 and decreases when the energy increases for $E>0.1$ eV/amu, while the Langevin model predicts a constant ratio of 1.4. These results qualitatively agree with the kinematic model of Ref. [26] at $E>0.1$ eV/amu, but not at lower energies where the semiclassical approximation of this model is probably not appropriate. It can be noted from Fig. 3 that the decrease due to the isotope effect does not significantly improves the agreement with the experimental results. Another possible explanation of the difference with the experiment could be an inaccurate treatment of transitions to other molecular states. In particular transitions to molecular states dissociating into $N^+(2s2p^3\ 3P^o)$, whose energies show avoided crossings with those of the molecular entrance channels at $R\simeq 11a_0$, should

become relevant at low velocities, but we have shown in Ref. [4] that they are not significant in the energy range of the experiment. Moreover, since those transitions take place at very large internuclear distances compared to that of the most important avoided crossing ($\approx 6.4a_0$), interferences between both are unlikely, so that transitions at distant avoided crossings increase the EC cross section, and cannot explain the discrepancy with the experimental data. On the other hand, the results of Fig. 4 suggest that a possible contamination by metastable ions would not be noticeable at $E < 10$ eV/amu.

To summarize, we report EC cross sections for collisions of O^{2+} and N^{2+} with $H(1s)$, by applying a molecular expansion in terms of multireference-CI wave functions, which allows us to cover a large energy range. In particular, low energy cross sections exhibit, for both systems, Langevin-type increases. We have corrected our previous results for $N^{2+}+H(1s)$ collisions, at energies between 0.1 and 0.3 eV/amu. Although our EC cross section for these collisions show a better qualitative agreement with merged-beams experiments than that of Ref. [4], some discrepancies remain in the low-energy region, where the experimental values depart from the $1/\sqrt{E}$ dependence found in all calculations at low energies. We have also shown the presence of resonant structures in the total EC cross section for both collision systems.

I.R. is grateful to the Spanish MCyT for a "Contrato Ramón y Cajal." P.B. is funded by an FPU grant of the Spanish MEC. This work has been partially supported by DGICYT Projects Nos. ENE2004-06266 and FIS2004-04145.

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