

Penning detachment from atomic clusters

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Theoretical cross-sections are presented for Penning detachment of negatively-charged sodium clusters, receiving their detachment energy from $\text{Na}^*(3p_0, ^2P)$. Two clusters are examined: Na_7^- and Na_{19}^- . Classical trajectories describe the relative motion of the colliding species. Kohn–Sham density functional theory in local approximation, with exchange, correlation, and self-interaction corrections, and a spherical jellium potential, describe the electrons involved in the transition. In the range of collision energies from 0.1 to 10 eV/amu, the cross-sections for Penning detachment are approximately 10^{-13} cm². This implies that Penning detachment may be an effective means to prepare neutral clusters from size-selected negative-ion clusters in the laboratory. © 1999 American Institute of Physics. [S0021-9606(99)01043-0]

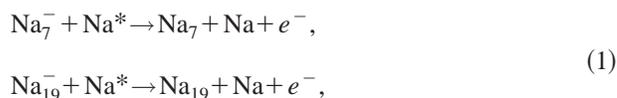
I. INTRODUCTION

Penning detachment (PD) is the process in which a negative ion A^- collides with an electronically excited energy donor N^* , the energy of excitation passes from the donor to the negative ion and sets the excess electron free, leaving as final products $A + N + e^-$. The process is so named by analogy with Penning ionization, the well-studied collision process, $A + N^* \rightarrow A^+ + N + e^-$. Typical cross-sections for Penning ionization are roughly like gas-kinetic cross-sections, of order 10^{-16} cm².^{1,2} Cross-sections for simple collisional detachment can be much smaller (see, e.g., Ref. 3 and references therein) because their magnitudes come largely from crossing-point interactions of potential curves for bound and free states of the *extra* electron. By contrast, early estimates⁴ of the cross-sections for Penning detachment indicated that these should be considerably larger than either of these, possibly even of the order 10^{-14} cm². More recent calculations discussed below have shown that the cross-sections for Penning detachment from atomic anions should indeed be at least this large for many states of the colliding species.^{5,6} Hence the process is tantalizing for study, even for this reason alone. Cross-sections this large imply that Penning detachment must play an important role in kinetics of almost any gaseous or plasma environment in which negative ions and excited atoms or molecules are both present. Nevertheless it has gone nearly unstudied until recently.^{7,8} Consistent with the large cross-sections, the detachment process is dominated by energy exchange when the distances between colliding partners is very large, so that the collision itself produces a minimal perturbation of the acceptor.

In two recent articles^{5,6} we presented the first theoretical

studies of Penning detachment to go beyond rough, order-of-magnitude estimates of the cross-sections for the process.⁴ That theoretical study was undertaken as a complement to experiments just beginning to search for PD as the theoretical studies started. The theory showed that PD is, in general, a very probable process and that it could be a very important mechanism to destroy negative ions in a variety of environments such as electric discharges and plasmas. This first stage of the research opened a number of new opportunities and possibilities for processes not yet observed, but with tantalizing potential. One in particular is the possibility of PD with negatively-charged clusters.

In this article we describe our study of neutralization of gaseous negatively-charged clusters by detachment caused by energy transfer from excited atoms. In particular, we will consider the reactions:



where Na^* is an excited sodium atom which acts as an energy donor. In this work we will consider the lowest $^2P_{1/2}([\text{Ne}]3p_0)$ state of sodium. Since PD is a very efficient yet “gentle” way to neutralize negatively-charged species, the above reactions may be very useful in producing neutral clusters of a single, selected number of atoms. In particular, the above reactions lead to open-shell Na_7 and Na_{19} clusters that are practically absent in the abundance spectra of sodium clusters.⁹ Mass selection of clusters is usually performed by mass-selecting charged precursors which, in many cases, are not stable and may fragment to yield a variety of

products. In contrast, the above negatively-charged clusters are generally more stable and easy to produce.¹⁰ However, apart from photodetachment,¹¹ virtually nothing was previously known—either from theory or experiment—about neutralization processes involving such negative clusters.

PD cross-sections are necessary inputs for describing the Penning detachment process for clusters, as well as for many other phenomena. To obtain PD cross-sections for the above reactions, one needs first a good electronic description of Na_7^- and Na_{19}^- . This is not an easy task due to the large number of active electrons (8 and 20, respectively) and to the importance of electron correlations. However, these are closed-shell metal clusters that can be reasonably described in the framework of the spherical jellium model.¹² Thus, we have used a Kohn–Sham formalism with a local density approximation which includes exchange, correlation, and a self-interaction correction. This provides a good representation of the isolated cluster and will be used as a starting point for the description of the PD process. Details of the method are given in Sec. II. The results form the subject of Sec. III, and Sec. IV summarizes the results and explores potential future implications and directions of Penning detachment from clusters.

II. THE METHOD

As will be discussed below (Sec. III), the excitation energy of $\text{Na}^*([\text{Ne}]3p_0)$ atoms (2.1 eV) is large enough to detach the outer electron of both Na_7^- and Na_{19}^- clusters; however, it is smaller than the energy needed to detach electrons from the inner shells. In addition, the sodium excitation energy is smaller than the energy required to excite the plasmon resonance of the clusters (the latter energy is 2.8 eV for the isoelectronic Na_{20} cluster and one would expect a similar value for Na_{19}^-).¹³ Thus, Penning detachment is essentially a two-electron process in which the energy of the excited electron of the Na atom is transferred to the loosely bound electron of negative clusters, the other electrons remaining passive during the collision. Therefore, the dynamics of the Penning detachment process can be studied using an effective two-electron Hamiltonian \mathcal{H}_{el} . The sodium valence electron is described using the same model potential as in our previous works.^{5,6} This potential has been widely used in the study of ion–atom collisions¹⁴ as well as in atomic structure calculations.¹⁵ We shall present now our description of the isolated cluster.

A. Cluster description

The cluster has been described using the theoretical method given in Refs. 16, 17. Briefly, we use the spherical background jellium model which consists in replacing the real ionic core potential by a constant positive background corresponding to a uniformly distributed charge density. In the Kohn–Sham formulation of density functional theory, the ground-state electronic density ρ_C of an N -electron system is written in terms of single-particle orbitals ϕ_i . These orbitals obey the Schrödinger equation

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{KS}}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}), \quad (2)$$

where $V_{\text{KS}}(\mathbf{r})$ is an effective single-particle potential given by

$$V_{\text{KS}}(\mathbf{r}) = V_{\text{jel}}(\mathbf{r}) + V_{\text{H}}(\rho_C(\mathbf{r})) + V_{\text{xc}}(\rho_C(\mathbf{r})), \quad (3)$$

with $V_{\text{H}}(\rho_C(\mathbf{r}))$ the Hartree potential and $V_{\text{xc}}(\rho_C(\mathbf{r}))$, the exchange–correlation potential. In this work, we have used the form obtained by Gunnarsson and Lundqvist¹⁸ in the framework of the local density approximation (LDA):

$$V_{\text{xc}}(\rho_C(\mathbf{r})) = -\left(\frac{3\rho_C(\mathbf{r})}{\pi}\right)^{1/3} - 0.0333 \log\left(1 + \frac{11.4}{r_s(\mathbf{r})}\right), \quad (4)$$

where $r_s(\mathbf{r}) = [3/4\pi\rho_C(\mathbf{r})]^{1/3}$ is the local Wigner–Seitz radius.

In the LDA approximation, the exchange contribution to V_{xc} decreases exponentially to zero at long distances. This unphysical behavior is corrected, following Perdew and Zunger,¹⁹ by adding a self-interaction correction (SIC) to the potential (we will call this method LDAXC-SIC). This procedure has been successfully applied to the study of both ground and excited state properties of small metal clusters.^{20–23} The corrected Kohn–Sham potential V_{SIC}^i is then given by

$$V_{\text{SIC}}^i(\mathbf{r}) = V_{\text{jel}}(\mathbf{r}) + \int \frac{[\rho_C(\mathbf{r}') - \rho_i(\mathbf{r}')]d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{xc}}[\rho_C(\mathbf{r})] - V_{\text{xc}}[\rho_i(\mathbf{r})], \quad (5)$$

where ρ_i is the i single-particle density. Notice that the potential V_{SIC}^i is now explicitly state-dependent.

Similar to the relation given by Koopman’s theorem in Hartree–Fock (HF) theory, the energy of the highest occupied (HO) orbital resulting from *exact* Kohn–Sham calculations is an excellent approximation to the cluster ionization potential (in our case, the cluster detachment energy). This means that the eigenvalue and eigenfunction associated with the HO orbital can be interpreted as the particle energy and wave function, respectively. Although this cannot be proved for other Kohn–Sham eigenvalues and eigenfunctions (see Ref. 12 for a detailed discussion), one can expect, however, this interpretation to provide reasonable approximations to the actual single-particle properties.

The V_{SIC}^i potentials of the isolated cluster have been obtained numerically using Eqs. (2) and (5). For practical reasons, we have fitted these potentials to linear combinations of 20 Gaussian functions placed on the cluster center. The resulting analytical potentials are virtually identical to the exact potentials to a precision of 10^{-3} a.u.

B. Cross-sections

We treat the problem semiclassically in this sense: the nuclei follow classical trajectories in the field induced by the effective interatomic potential whereas the electrons are described quantum-mechanically. The initial state of the system $\text{Na}_n^- + \text{Na}^*$, ψ_0 , is embedded in the electronic continuum of the molecular negative ion Na_nNa^- formed during

TABLE I. Eigenenergies (in eV) of the occupied single particle states of Na_7^- and Na_{19}^- calculated in the local density approximation with exchange, correlation, and self-interaction correction (LDAXC-SIC, see text).

Orbital	Na_7^-	Na_{19}^-
1s	3.3	4.1
1p	1.6	3.2
1d		2.1
2s		1.6

the collision. With this picture in mind, we define a basis of states as follows. Bound electronic states for $t = -\infty$ are formally the solutions of

$$(Q\mathcal{H}_{\text{el}}Q - E_i)\psi_i = 0, \quad (6)$$

and (unbound) electronic continuum states are the solutions of

$$(P_{\nu l}\mathcal{H}_{\text{el}}P_{\nu l} - E)\psi_{E,\nu l} = 0, \quad (7)$$

where ν represents the set of quantum numbers describing the final state of the target, l is the angular momentum of the ejected electron, and $P_{\nu l}$ and Q are projection operators that satisfy the exclusionary conditions:

$$P_{\nu l}P_{\nu' l'} = \delta_{\nu\nu'}\delta_{ll'}, \quad (8)$$

$$P = \sum_{\nu} \sum_l P_{\nu l}, \quad (9)$$

$$PQ = 0, \quad (10)$$

$$P + Q = 1, \quad (11)$$

for all R . The effective two-electron Hamiltonian is written as

$$\begin{aligned} \mathcal{H}_{\text{el}} = & -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + V_{\text{SIC}}(1) + V_{\text{SIC}}(2) + V_{\text{Na}}(1) \\ & + V_{\text{Na}}(2) + \frac{1}{r_{12}}, \end{aligned} \quad (12)$$

where V_{SIC} (V_{Na}) is the cluster (atom) potential described above for the outer electron.

As in Refs. 5, 6, we use the local approximation to evaluate the total Penning detachment cross-sections. In this approximation, the total ionization probability for a given nuclear trajectory can be written

$$P(b) = 1 - \exp\left(-2 \int_{R_0}^{\infty} \Gamma(R)/v(R) dR\right), \quad (13)$$

where $\Gamma(R)$ is the total width of the ψ_0 state

$$\Gamma(R) = 2\pi \sum_{\nu} \sum_l |\langle \psi_0 | Q\mathcal{H}_{\text{el}}P_{\nu l} | \psi_{E=E_0,\nu l} \rangle|^2, \quad (14)$$

$v(R)$ is the radial velocity of the nuclei

$$v(R) = v_0 \sqrt{1 - \frac{2V(R)}{\mu v_0^2} - \frac{b^2}{R^2}}, \quad (15)$$

and R_0 is the classical turning point (note that the previous equation was misprinted in Refs. 5, 6). $V(R)$ is the inter-

atomic potential [i.e., the lowest eigenvalue in Eq. (6)], μ is the reduced mass of the nuclei, v_0 the initial velocity, and b the impact parameter. The total detachment cross-section is given by

$$\sigma = 2\pi \int_0^{\infty} 2bP(b)db. \quad (16)$$

The factor of 2 inside the integral appears because the detached electron can be either the α or β electron occupying the $m=0$ orbital of the cluster outer shell.

C. P and Q wave functions

The Q -states are obtained by diagonalizing $Q\mathcal{H}_{\text{el}}Q$ in a basis of (properly antisymmetrized) two-electron configurations of the form $\{\varphi_0-\varphi_{k_{\text{Na}}}\}$, where φ_0- is the HO one-electron orbital of the anion

$$(-\frac{1}{2}\nabla^2 + V_{\text{SIC}})\varphi_0- = \epsilon_0\varphi_0-, \quad (17)$$

and the $\varphi_{k_{\text{Na}}}$ orbitals are the solutions of

$$(-\frac{1}{2}\nabla^2 + V_{\text{Na}})\varphi_{k_{\text{Na}}} = \epsilon_{k_{\text{Na}}}\varphi_{k_{\text{Na}}}. \quad (18)$$

Two-electron configurations with both electrons in Na are not included in the diagonalization procedure, since their contribution to the Penning detachment process is expected to be small. The φ orbitals are written as linear superpositions of Gaussian-type orbitals (GTO). The orbitals included in the present calculations are $\varphi_{k_{\text{Na}}} = 3s, 3p, 3d, 4s, 4p, 4d, 5s, 5p, 5d,$ and $6s$ for Na.

The P -states are (properly antisymmetrized) two-electron configurations of the form $\tilde{\psi}_{E,l} = \tilde{\varphi}_{\epsilon,l}\varphi_{\nu_{\text{Na}}}$, where $\varphi_{\nu_{\text{Na}}}$ is the valence orbital of the neutral and the $\tilde{\varphi}_{\epsilon,l}$ functions are discretized continuum orbitals of the negatively-charged cluster. The latter correspond to those solutions with energies lying above the ionization threshold and are obtained by diagonalizing Eq. (17) using an even-tempered sequence of GTO for each l . The discretized electronic continuum thus obtained is handled as in Ref. 5.

III. RESULTS AND DISCUSSION

The electronic configurations of Na_7^- and Na_{19}^- are, respectively, $1s^21p^6$ and $1s^21p^61d^{10}2s^2$. The calculated orbital energies arising from the solution of the Kohn–Sham Eq. (2) including the SIC correction defined in Eq. (5) are given in Table I. From this table we can see that the energies required to detach a $1p$ electron from Na_7^- or a $2s$ electron from Na_{19}^- are roughly the same (≈ 1.6 eV). We are not aware of experimental electron affinities of Na_7 and Na_{19} to compare with. However, they are available for K_7 and K_{19} , which are 1.1 and 1.3 eV, respectively.²⁴ The theory of Sec. II A leads to 1.4 eV for both potassium clusters and we expect a similar degree of accuracy in the case of the two sodium clusters investigated here. As expected, the approximation is worse for the smaller cluster because the jellium model is less appropriate. As mentioned above, the excitation energy of $\text{Na}^*([\text{Ne}]3p_0)$ is 2.1 eV, which is large

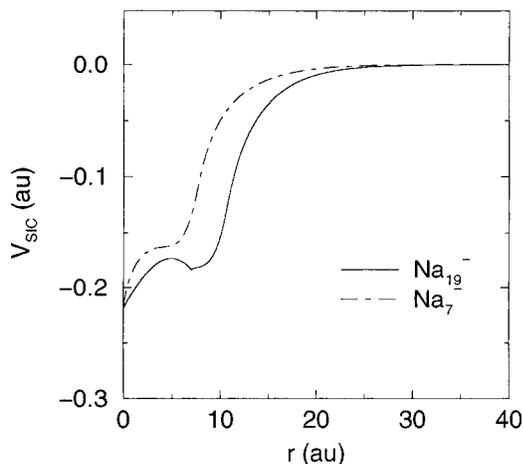


FIG. 1. Cluster potentials V_{SIC} as functions of the distance to the cluster center.

enough to detach an electron from the cluster outer shell of both Na_7^- and Na_{19}^- , but is smaller than the energy required to detach electrons from the inner shells (see Table I). This supports our previous assumption that Penning detachment is essentially a two-electron process (see the preceding section), except for (maybe) the $1d$ electrons of Na_{19}^- whose energy is very close to the sodium excitation energy.

In Fig. 1, we compare the potentials of Na_7^- and Na_{19}^- . As mentioned in Sec. II A, the potentials resulting from Eq. (5), V_{SIC}^i , are state-dependent. Figure 1 shows an average potential defined as

$$V_{\text{C}}(r) \equiv \langle V_{\text{SIC}}(r) \rangle = \frac{1}{N} \sum_k V_{\text{SIC}}^k(r) n_k, \quad (19)$$

where the summation is performed over all occupied orbitals and n_k denotes the number of electrons in subshell k . These potentials extend well outside the jellium spheres used in the corresponding calculations. Indeed, from the well-known formula $R_{\text{C}} = r_s n^{1/3}$, the radii of these jellium spheres are, respectively, $R_{\text{C}} = 7.65$ and 10.67 a.u., and the potentials are far from negligible for $r > R_{\text{C}}$. This is due to electron spill out and has important consequences on the value of the calculated cross-sections.

In order to evaluate the Penning detachment cross-sections, we have included $l=0$, $l=1$, and $l=2$ continuum states in the Na_7^- case, but only $l=0$ and $l=1$ continuum states in the Na_{19}^- case. Indeed, as explained in Ref. 5 and will be shown below, due to the long-range nature of the Penning detachment process, the dipole-dipole term of the multipolar expansion of $1/r_{12}$ is responsible for most of the relevant couplings of the process. Since the ejected electrons initially occupy the $1p$ and $2s$ orbitals for Na_7^- and Na_{19}^- , respectively, electrons will be mostly ejected into continuum orbitals with $l=0$ and 2 (Na_7^-), and $l=1$ (Na_{19}^-). Higher angular momenta lead to a redistribution of the final state population but barely affect the value of the total cross-section (see Ref. 5).

Figure 2 shows the transition probability times impact parameter as a function of impact parameter for the $\text{Na}_7^- + \text{Na}^* \rightarrow \text{Na}_7 + \text{Na} + e^-$ reaction at 1 eV/amu impact energy.

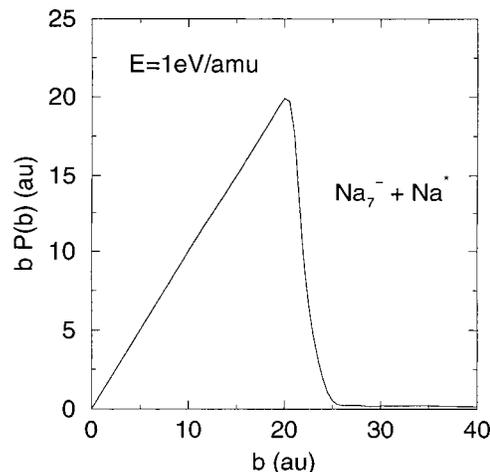


FIG. 2. Transition probability times impact parameter as a function of impact parameter for the Penning detachment reaction $\text{Na}_7^- + \text{Na}^*([\text{Ne}]3p_0) \rightarrow \text{Na}_7 + \text{Na} + e^-$ at 1 eV/amu impact energy.

The transition probability is practically equal to one for $b < 20$ a.u. and decreases abruptly in the interval $b = 20-25$ a.u. These values of b are much larger than the cluster radius, thus showing that the Penning detachment process takes place far from the cluster surface. This long range behavior has been also observed in the case of Penning detachment from H^- ions.^{5,6} Similar qualitative conclusions are valid for other impact energies and for Na_{19}^- ions.

The calculated Penning detachment cross-sections are shown in Fig. 3. They decrease with impact energy and are of the order of 10^{-13} cm^2 in the whole energy range investigated here. These cross-sections are roughly an order-of-magnitude larger than the corresponding geometrical cross section, πR_{C}^2 , which are also shown in the figure. The cross-sections for Na_7^- are smaller than for Na_{19}^- . Therefore, the fact that two partial waves ($l=0,2$) are dominant in the first case, while only one ($l=1$) is dominant in the second case does not have a significant influence.

Figure 3 also includes the results of Ref. 5 for the $\text{H}^- + \text{Li}^*(2p)$ collision. Although the latter cross-sections are

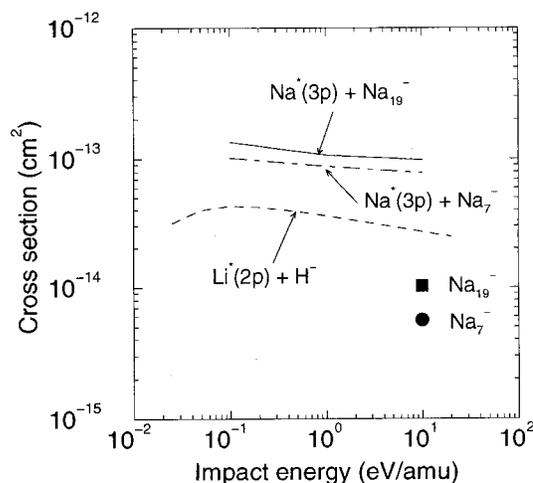


FIG. 3. Penning detachment cross-sections as functions of impact energy. The circle and the square are geometrical cross-sections (see text).

significantly smaller, the general behavior with impact energy is roughly the same. Now, Fig. 3 shows that the relative increase of the cross-section from H^- to Na_7^- , and from the latter to Na_{19}^- is smaller than expected from purely geometrical considerations. In fact, the critical parameter is not only the ion size but also the excess energy of the ejected electron. From Table I and Ref. 5, the values of the excess energies are 1.1 eV for $H^- + Li^*(2p)$ and 0.5 eV for both $Na_7^- + Na^*(3p)$ and $Na_{19}^- + Na^*(3p)$. As explained in Ref. 5, the larger the excess energy, the smaller is the cross-section. Thus, the size effect is partially damped because the excess energy is practically the same for the two clusters investigated here.

IV. CONCLUSION

Penning detachment of electrons from negatively-charged clusters appears to offer an effective means to prepare neutral clusters from their negative-ion precursors. The cross-sections are even larger than those for Penning detachment from atomic ions, but only about as much greater as one might expect from the geometric cross-sections of the ions. As with atomic ions, the energy exchange occurs predominantly when the donor and acceptor are far apart, relative to their geometric cross-sections.

One issue not discussed here but of immediate concern for potential experiments is the question of whether the electrons being detached would scatter inelastically in the clusters before they escape, possibly losing so much of their energy that they remain trapped and the energy from the donor goes into evaporation of one or more atoms. Negative clusters in which the excess electron is predominantly on the surface are unlikely to have this complication, but clusters in which the excess electron is in an interior "bubble" may exhibit evaporation (dissociation) when they absorb energy from an electronically excited donor.

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