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Controlled formation of weakly bound atomic negative ions by electron transfer from state-selected Rydberg atoms

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Abstract. – Using crossed atomic beams and mass spectrometric ion detection we have studied the formation of negative Ca ions in slow collisions between laser-excited state-selected $\text{Ne}^{**}(ns, J = 2)$ and $\text{Ne}^{**}(nd, J = 4)$ Rydberg atoms and ground state Ca atoms. The rate coefficients exhibit resonant behaviour with maxima at an effective principal quantum number n^* of about 11.5 and an estimated peak value of about $10^{-8} \text{ cm}^3 \text{ s}^{-1}$. Two different theoretical calculations, based on a curve-crossing model and on a modified adiabatic theory, respectively, yield n^* -dependences of the rate coefficients in good agreement with the experimental results.

The negative ions of Ca, Sr, and Ba have received a lot of attention over the last ten years [1]-[8] as prototype examples of weakly bound systems whose stability is determined by intricate electron correlation effects. Precise experimental values of their binding energies have only very recently become available through a combination of laser photodetachment with resonance ionization spectroscopy [6]-[8]. For Ca^- , for example, the binding energies were determined as 24.55(10) meV for $\text{Ca}^-(^2P_{1/2})$ and 19.73(10) meV for $\text{Ca}^-(^2P_{3/2})$ [7]. In most experiments these weakly bound atomic negative ions are produced by passage of the respective positive ions at keV energies through an appropriate gaseous target [1]. Recently, McLaughlin and Duquette [9] indicated an alternative route towards the production of Ca^- ions: studying ion formation in $\text{Ca}^{**}(nd) + \text{Ca}$ collisions at thermal energies, they reported a sharp peak in both Ca^+ and Ca^- production at $n = 25$, corresponding to an effective principal quantum number of $n^* = 23.9$. Using a generalization of the quasi-free-electron model, Fabrikant [10] interpreted these results in terms of a resonant electron transfer process in which the Rydberg binding energy $E_0/2n^{*2}$ ($E_0 = 27.21 \text{ eV}$) essentially matches the electron affinity for Ca; the experimental peak location ($n^* = 23.9$) suggested $\text{EA}(\text{Ca}) = 24(1) \text{ meV}$ in contrast to the then

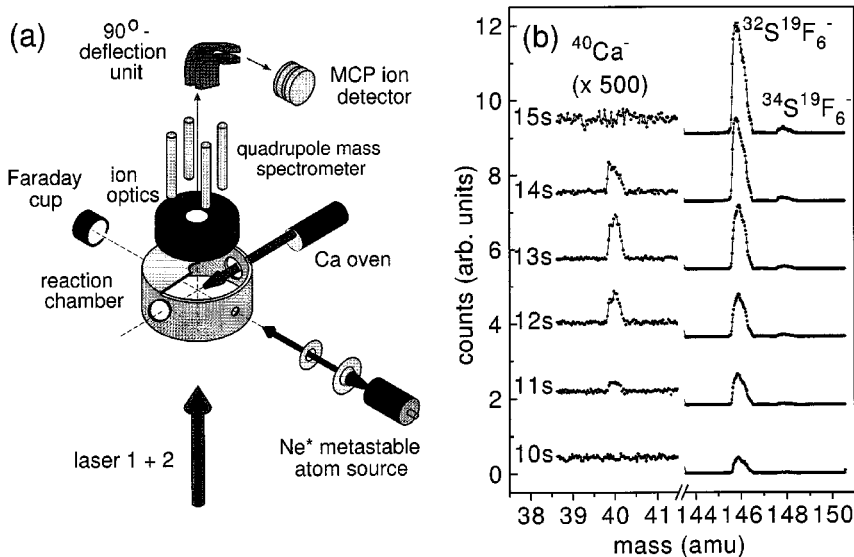


Fig. 1. – (a) Experimental setup for mass spectrometric studies of Ca^- formation in thermal energy collisions of laser-excited $\text{Ne}^{**}(ns, nd)$ Rydberg atoms with Ca atoms. (b) n -dependent negative ion mass spectra resulting from collisions of state-selected $\text{Ne}^{**}(ns)$ Rydberg atoms with Ca atoms. For clarity, the zero intensity line of the consecutive mass spectra has been shifted.

accepted value $\text{EA}(\text{Ca}) = 18.4(25)$ meV [1]. In this context the recent studies of Desfrancois *et al.* [11]–[13] on the controlled production of dipole-bound molecular negative ions XY^- with binding energies in the range from 20 meV to below 1 meV are of great interest. Using electron transfer from state-selected $\text{Xe}^{**}(nf)$ Rydberg atoms, they found resonant behaviour of the n -dependent rate coefficients $k_{nl} = \langle \sigma_{nl} v_{\text{rel}} \rangle$ (*i.e.* the product of the cross section with the collision velocity averaged over the experimental velocity distributions) for XY^- formation. From their data they determined a simple empirical relation between the binding energy EA of the XY^- ion and the value of the (effective) principal quantum number n_{max}^* for which the cross section attains its maximum, namely $n_{\text{max}}^* = (23 \text{ eV}/\text{EA})^{(1/2.8)}$ [11], [13]. For an electron affinity EA of 20 meV, for example, the maximum is expected to occur at $n_{\text{max}}^* = 12.4$ in obvious contrast to the findings of McLaughlin and Duquette [9]. Lorensen *et al.* [14] have recently demonstrated that Ca^+ formation following excitation of $\text{Ca}^{**}(25d)$ with the scheme used in [9] is in fact due to a resonant atomic three-photon ionization process and therefore not the result of $\text{Ca}^{**}(25d) + \text{Ca}$ collisions. In the meantime Khrebtukov and Fabrikant [15] developed an improved theoretical model for the description of negative ion formation through Rydberg electron transfer. Using $\text{EA}(\text{Ca}) = 18.4$ meV and the experimental conditions of the single-beam experiment in [9], they predicted resonant behaviour of the Ca^- production cross section with a maximum at about $n^* = 10.2$ (fig. 6 in [15]). In this letter we report new experimental results for Ca^- formation in collisions between ground state Ca atoms and state-selected $\text{Ne}^{**}(ns)$ and $\text{Ne}^{**}(nd)$ Rydberg atoms. We find resonant behaviour of the rate coefficients with a peak at an effective principal quantum number of about $n^* = 11.5$. For comparison and interpretation we have carried out calculations which are based on two different theoretical approaches [13], [15].

In our experiment (fig. 1 (a)) a collimated metastable $\text{Ne}^*(3s^3P_{2,0})$ atom beam, originating from a differentially pumped dc discharge source, is crossed by a collimated Ca beam produced

under effusive conditions in a differentially pumped, resistively heated oven. The Ne^* beam has supersonic character with an average velocity of about 930 m/s and a velocity width of about 35% (FWHM). The Ca beam is Maxwellian with a temperature of about 1100 K. In the crossing region of the two beams their densities amount to about $2 \times 10^6 \text{ cm}^{-3}(\text{Ne}^*)$ and $6 \times 10^9 \text{ cm}^{-3}(\text{Ca})$. $\text{Ne}^{**}(ns, J = 2; \text{ quantum defect } \mu_s = 1.32 \text{ [16]})$ or $\text{Ne}^{**}(nd, J = 4; \mu_d = 0.02 \text{ [16]})$ Rydberg states are produced in a controlled way by two-step transverse laser excitation of the $\text{Ne}^*(^3P_2)$ atoms via the intermediate $\text{Ne}^*(3p\ ^3D_3)$ level [16], [17]; a single-mode ring dye laser, which is locked to the atomic transition (640.4 nm) by polarization spectroscopy in an rf discharge, is used for the first step (640.4 nm) and a stabilized single mode dye laser (Stilben 3, 420–460 nm) for the second transition. Mass spectra of positive ions (resulting from Penning ionization, PI) and of negative ions due to the reactions $\text{Ne}^{**}(n\ell) + \text{Ca} \rightarrow \text{Ne}^+ + \text{Ca}^-$ are measured with a quadrupole mass spectrometer (Balzers), equipped with a dual channel plate detector. For calibration purposes SF_6 gas is injected into the reaction region through a conical nozzle surrounding the Ca beam; the SF_6 density amounted to about $2 \times 10^{11} \text{ cm}^{-3}$. The n -dependent rate coefficients for SF_6^- formation in the electron transfer reactions $\text{Ne}^{**}(ns, nd) + \text{SF}_6 \rightarrow \text{Ne}^+ + \text{SF}_6^-$ are rising towards higher n in the range of interest and are known from previous work [17], [18]. With this knowledge we determine relative rate coefficients for Ca^- production from the n -dependent, mass-analyzed signals for Ca^- and SF_6^- shown for $\text{Ne}^{**}(ns)$ collisions in fig. 1 (b). We note that the SF_6^- intensities in fig. 1 (b) have been normalized such that they mirror the n -dependence of the known rate coefficients [17]. Therefore the Ca^- intensities reflect in a direct way the respective variation of the rate coefficient which exhibits resonant behaviour with a maximum at $n = 13$ ($n^* = 11.68$). Analogous data have been obtained for $\text{Ne}^{**}(nd)$ collisions; the n^* -dependence is very similar with the maximum occurring at about $n^* = 11.5$. Figure 2 summarizes the experimental data and compares them with the results of theoretical calculations to be discussed below. Our results are at variance with the experiments of McLaughlin and Duquette [9]. We find the maximum rate coefficient —consistently for $\text{Ne}^{**}(ns)$ and $\text{Ne}^{**}(nd)$ electron transfer— at an effective principal quantum number of about 11.5 which is quite close to the value expected from the empirical formula due to Desfrancois *et al.* [11], [13]. The ratio of the peak rate coefficients is determined as $k_{13s}/k_{12d} = 1.5$. Using the experimentally known Ca and SF_6 densities in conjunction with the measured value for SF_6^- formation of $k_{13s} = 8.6 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ ($\pm 50\%$) [17] and assuming equal overall detection efficiencies for Ca^- and SF_6^- ions, we estimate the absolute value of the 13s rate coefficient for Ca^- formation as $k_{13s} = 1 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ (to within a factor of three).

For comparison with our experimental results we have carried out calculations of the Ca^- production cross sections as a function of n^* and of collision velocity v_{rel} using i) a parameter-free curve crossing model [13] and ii) an extended version of a modified adiabatic theory [15] (atomic units are used in the following expressions). In model i) the cross section for negative ion formation is given by $\sigma_{n\ell}(v_{\text{rel}}) = 2\pi \int_0^{R_c} P(b) b db$, where $R_c = (1/2n^{*2} - EA)^{-1}$ is the crossing radius between the initial (flat) covalent and the ionic curve and $P(b)$ represents the impact parameter dependent probability for ion pair formation. In the two-channel case we simply have $P(b) = 2p_{ci}(1 - p_{ci})$ with the Landau-Zener probability p_{ci} for switching from the covalent channel (c) to the final ionic channel (i) given by $p_{ci} = 1 - \exp[-2\pi H_{ci}(R_c)^2 R_c^2 / v_r(R_c, b)]$, where v_r denotes the radial velocity and H_{ci} is the exchange coupling element which is given by $H_{ci}(R_c) = (N_i/2) f_{ci} X_{n\ell}(R_c)$ [13], [19]. N_i represents the normalization constant of the electron wave function in the negative ion (for the definition of N_i see [13], [19]). $X_{n\ell}(R_c)$ is the value of the unperturbed radial wave function of the Rydberg electron at $r = R_c$. The factor f_{ci} depends on the orbital angular momenta ℓ , ℓ_i and their common projection ($m = m_i$) on the internuclear axis (for Ca^- , $\ell_i = 1$, $m_i = 0, 1$),

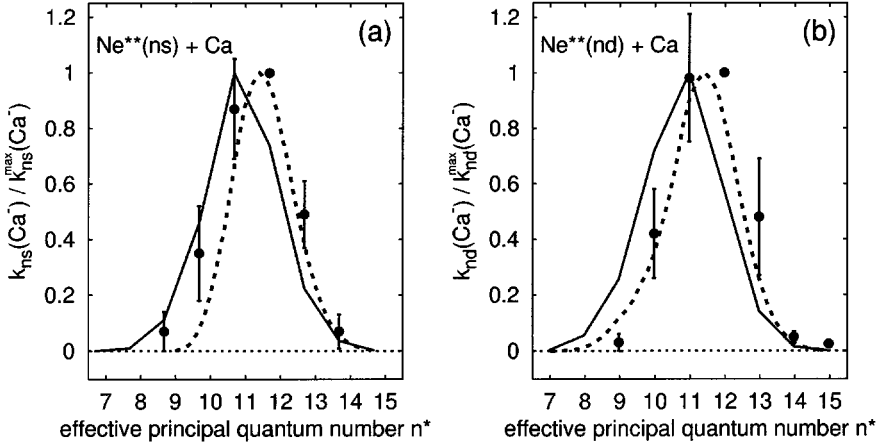


Fig. 2. – Comparison of experimental and theoretical results for the relative n -dependent rate coefficients $k_{nl}(\text{Ca}^-)$ for Ca^- formation in thermal energy collisions of state-selected $\text{Ne}^{**}(n\ell)$ Rydberg atoms with Ca atoms: (a) $\text{Ne}^{**}(\text{ns}) + \text{Ca}$. (b) $\text{Ne}^{**}(\text{nd}) + \text{Ca}$. Solid lines: curve crossing model. Dashed lines: modified adiabatic theory. Filled circles with error bars: experimental data (average of three data runs in both cases).

i.e. $f_{ci} = (3(2\ell + 1))^{1/2}$ for $m = 0$, $f_{ci} = (6\ell(\ell + 1)(2\ell + 1))^{1/2} / (2R_c(2EA)^{1/2})$ for $m = 1$, and $f_{ci} = 0$ for $m > 1$ [13], [19]. Realistic Ca^- wave functions were calculated on the basis of a model potential with appropriate long-range behaviour $1/r^2 - \alpha/2r^4$ ($\alpha = \text{Ca}$ polarizability = 159 au [20]) and was chosen to yield the proper Ca electron affinity; somewhat dependent on the choice of the potential we found $N_i = 0.117$ for $\text{Ca}^-(^2P_{3/2})$ and $N_i = 0.132$ for $\text{Ca}^-(^2P_{1/2})$ (within 5%). We assume that the $\text{Ne}^+(^2P_{3/2})$ core acts as spectator and can be considered as fixed in the electron transfer process. The effects of multiple crossings associated with $n\ell$ Rydberg levels other than that of the entrance channel were included as described in [13]. Separate calculations with only one ionic channel $\text{Ne}^+(^2P_{3/2}) + \text{Ca}^-(^2P_J)$, using the appropriate electron affinities for $J = 1/2$ or $J = 3/2$, showed similar n -dependences with maxima at n^* which were lower for $J = 1/2$ by about one unit. Both final ionic channels were taken into account in a coupled channel calculation ignoring all interference effects. Carrying out the average over the experimental collision velocity distribution we obtain rate coefficients for Ca^- formation in $\text{Ne}^{**}(n\ell) + \text{Ca}$ collisions as shown by the solid lines in fig. 2. They reproduce the n^* -dependence of the experimental data in a satisfactory way; the predicted peak position is located at a somewhat smaller n^* than the experimental value. The calculated peak rate coefficients of $k_{13s} = 1.7 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ and $k_{12d} = 0.82 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ agree with the estimated experimental values.

We also carried out calculations using a new version of the modified adiabatic theory which differs from that in [15] in two aspects. First, it incorporates the polarization attraction in the $e^- + \text{Ca}$ system. Second, it takes into account the decay of the formed negative ion due to the Coulomb field of the positive ion in a form proposed by Radtsig and Smirnov [21]. For the decay width we use theoretical results [22] which take into account the polarization potential of Ca . This decay is equivalent to the multiple crossing effect mentioned above where intersection with each sublevel of the degenerate Coulomb manifolds leads to the loss of flux from the ionic channel. To account for the Ca^- fine structure two calculations were carried out with the appropriate electron affinities, and the resulting cross sections were averaged

according to the statistical weights of the Ca^- states. Our modified adiabatic theory yields n^* -dependences (dashed lines in fig. 2) which show good overall agreement with the experimental results; the absolute values of the calculated rate coefficients ($k_{13s} = 0.90 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$, $k_{12d} = 0.71 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$) agree with those of the curve crossing model to within 50% and with the experimental estimates within the uncertainties of the latter. We note that in all the calculations it is assumed that the ionic complex $\text{Ne}^+ + \text{Ca}^-$ is not lost to the autoionization continuum (formation of $\text{Ne} + \text{Ca}^+ + e^-$ in a Penning ionization type process) to which it is expected to be strongly coupled at short internuclear distances $R < 10a_0$ [20]. Estimates of the fraction of those collisions which reach such small distances show that loss due to autoionization should be less than about 10% and, therefore, only a small effect. From an experimental point of view, Ca^- ions are subject to losses caused by blackbody-radiation-induced photodetachment [23] over the time interval from their creation to detection. In our experiment this interval amounts to about 76 μs , corresponding to photodetachment probabilities of about 15%.

We conclude that we have observed resonant behaviour of the n^* -dependent rate coefficients measured for Ca^- production in slow collisions of state-selected Ne^* Rydberg states with Ca atoms. The n^* -dependence is well recovered in two different calculations with a parameter-free curve crossing model and a modified adiabatic theory, respectively. The former has previously been found adequate for the description of Rydberg electron transfer to dipole-bound molecular negative ions [11]-[13]. We note that the situation for electron transfer from a Coulombic potential (*i.e.* from a Rydberg orbit) into a dipole-bound orbital (such as in CH_3CN^-) is quite different from that for formation of a weakly bound atomic negative ion such as Ca^- . For the former the effective potential for the active electron along the line connecting the Rydberg core and the target dipolar molecule exhibits a broad maximum between the nuclear centers, with an energy close to the Rydberg binding energy when the system is close to the crossing radius for the entrance channel with n_{max}^* [11]. In contrast $\text{Ca}^- (^2P_J)$ formation involves penetration of the centrifugal barrier associated with the $\ell_i = 1$ symmetry (with our model potential we find a barrier height of about 0.1 eV at an electron-Ca distance of about $11.6a_0$). This difference between the two cases is reflected in the respective size of the normalization factor of the radial wave function of the weakly bound electron. Correspondingly, the peak of the n -dependent rate coefficient for Ca^- formation occurs at a somewhat smaller value of the effective principal quantum number.

In future studies we plan to carry out experiments at higher collision energies and to investigate Rydberg electron transfer to other atoms with weakly bound negative ions (*e.g.*, Sr and Yb) to shed more light on the systematic changes of the electron transfer process with the binding energy. The case of Yb promises to be particularly interesting as a model system since the Yb atom is expected to have only one bound negative ion state with an electron affinity below 20 meV [24]-[26].

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